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TRANSACTIONS.

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TRANSACTIONS.

I.—*Azomethine Derivatives of the 2- and 4-Hydroxy-α-Naphthaldehydes.*

By GILBERT T. MORGAN and HARRY GORDON REEVES.

THE analogy between azo- and azomethine-compounds was first pointed out by Weil (*Ber.*, 1894, **27**, 3317) and afterwards further examined by Möhlau (*Ber.*, 1895, **28**, 324; 1898, **31**, 2250), who prepared, from *p*-nitrobenzaldehyde and three of the amino-naphthols, Schiff condensation products having the formula $NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot C_{10}H_6 \cdot OH$, and corresponding with the benzene-azo-α- and -β-naphthols, $NO_2 \cdot C_6H_4 \cdot N{:}N \cdot C_{10}H_6 \cdot OH$.

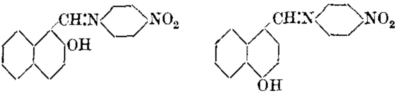
On investigating the solubility of *p*-nitrobenzylidene-4-amino-α-naphthol, Möhlau found that this azomethine compound resembled *p*-nitrobenzeneazo-α-naphthol in dissolving readily in cold dilute aqueous sodium hydroxide; *p*-nitrobenzylidene-1-amino-β-naphthol dissolved rather more sparingly in aqueous sodium hydroxide, whereas *p*-nitrobenzylidene-2-amino-α-naphthol was almost insoluble in this reagent. The last azomethine derivative accordingly resembles in this respect *p*-nitrobenzeneazo-β-naphthol (para-red), which owes its technical application largely to its insolubility in aqueous alkalis.

From these experimental results, Möhlau inferred that the marked difference between the ortho- and para-series of azonaphthols subsists to a certain extent in the case of the corresponding azomethine compounds, $NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot C_{10}H_6 \cdot OH$. We have now carried this comparison between azo- and azomethine-compounds

a stage further by examining the reactions of a series of Schiff condensation products having the general formula

$$NO_2 \cdot C_6H_4 \cdot N{:}CH \cdot C_{10}H_6 \cdot OH.$$

The members of the new series, which are isomeric with Möhlau's compounds, contain the azomethine chromophore reversed, as shown in formulæ I and II; they are prepared by condensing the nitroanilines with 2- and 4-hydroxy-α-naphthaldehydes, the products obtained from *p*-nitroaniline having the following constitutions:

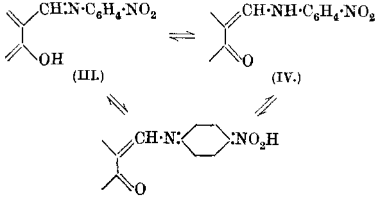


(I.) (II.)

4-*Hydroxy-α-naphthylidene*-p-*nitroaniline* (II) is very sparingly soluble in cold aqueous sodium hydroxide, but its isomerides from 4-hydroxy-α-naphthaldehyde and *o*- and *m*-nitroanilines dissolve readily in cold 10 per cent. sodium hydroxide, giving yellow solutions of the alkali salts, which slowly undergo hydrolysis into the generators of the azomethine compounds.

2-*Hydroxy-α-naphthylidene*-p-*nitroaniline* (I) and its two isomerides from *o*- and *m*-nitroanilines and 2-hydroxy-α-naphthaldehyde are insoluble in cold aqueous sodium hydroxide solution. As in the similar case of *p*-nitrobenzeneazo-β-naphthol, the acidic character of the hydroxyl group is diminished very appreciably by its proximity to the azo- or azomethine-chromophore. This analogy is not, however, very close, for under more drastic treatment with stronger aqueous or alcoholic alkali hydroxide the *o*-hydroxy-azomethine compounds undergo hydrolysis into their generators.

The diminution in acidic character of the *o*-hydroxy-azomethine compounds may result from a quinonoid rearrangement corresponding with that assumed to occur in the azo-β-naphthols in order to account for their insolubility in alkalis.



(III.) (IV.) (V.)

It is noteworthy that with azomethines derived from *o*- and *p*-nitroanilines a double quinonoid change is possible. The latter configuration (V) would account for the more intense colorations developed by the *ortho*- and *para*-nitro-compounds in alcoholic sodium hydroxide solution or in concentrated sulphuric acid. Apart from these colour changes and the difference in solubility, the hydroxy-azomethine compounds have the general properties of Schiff bases in regard to the action of hydrolytic agents and in the formation of additive compounds.

One very distinctive property of the aromatic azomethine compounds is their capacity for combining additively with anhydrous hydrogen cyanide (von Miller and Plöchl, *Ber.*, 1892, **25**, 2056; 1898, **31**, 2699). This tendency is diminished appreciably by the presence of acidic substituents in one or other of the two aromatic nuclei (Eibner, *Annalen*, 1898, **302**, 335), and sometimes the presence of nitro-groups inhibits the reaction completely (Morgan, T., 1900, **77**, 1210). In the present investigation, this addition of hydrogen cyanide was achieved in every instance, although it was found that the reaction occurred much more slowly with the *para*-nitro-compounds (I and II) than with their *o*- and *m*-isomerides. This difference in reactivity is probably due to more sparing solubility, which in turn would hinder the reversal of the dynamic changes indicated by formulæ III to V.

EXPERIMENTAL.

Preparation of 2- and 4-Hydroxy-α-naphthaldehydes (compare Gattermann, *Ber.*, 1899, **32**, 284; Morgan and Vining, T., 1921, **119**, 177).—One part of recrystallised α- or β-naphthol was added to a solution of freshly-prepared anhydrous zinc chloride (one part) in three parts of dry ether, hydrogen chloride was slowly introduced, and 10 c.c. of anhydrous hydrocyanic acid were added with continuous stirring. A clear, colourless solution was obtained which gradually assumed a greenish-yellow tint with α- or a clear yellow tint with β-naphthol, and ultimately became pasty owing to the separation of the aldimine hydrochloride. After twelve hours, this product was collected and hydrolysed with water, when the corresponding aldehyde was obtained; it was characterised by the formation of the Schiff base with aniline.

I. *Azomethine Derivatives from 2-Hydroxy-α-naphthaldehyde.*

An alcoholic solution containing 2-hydroxy-α-naphthaldehyde and the nitroaniline in molecular proportions, after heating in a

reflux apparatus for an hour, deposited on cooling a crystalline precipitate of the azomethine derivative, which was purified by crystallisation from the same solvent.

$HO{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO_2$.	Appearance.	M.p.	Requires N = 9·59 per cent.
2-Hydroxy-α-naphthylidene-o-nitroaniline	Lustrous, scarlet plates.	172°	Found : N = 9·70.
2-Hydroxy-α-naphthylidene-m-nitroaniline	Felted, orange needles.	165—166°	,, N = 9·65.
2-Hydroxy-α-naphthylidene-p-nitroaniline	Intensely crimson needles.	213°	,, N = 9·49.

Weighed quantities (0·02 to 0·05 gram) of the three isomerides were left in contact with 5 c.c. of cold 10 per cent. aqueous sodium hydroxide for one hour; the material in each case recovered unchanged without loss of weight gave the correct melting point, thus indicating an entire absence of solubility or of hydrolytic change. The three isomerides (*o*-, *m*-, and *p*-) dissolved in alcoholic sodium hydroxide, giving respectively yellow, orange-yellow, and crimson colorations which faded slowly to a pale yellow; they developed yellow colorations in concentrated sulphuric acid.

Addition of Hydrogen Cyanide to the Azomethine Derivatives of 2-Hydroxy-α-naphthaldehyde.

Excess of anhydrous hydrogen cyanide was added to the powdered azomethine compound, and the mixture was left in a cooled stoppered bottle with occasional shaking.

Phenylamino-2-hydroxy-α-naphthylacetonitrile,

$$C_6H_5{\cdot}NH{\cdot}CH(CN){\cdot}C_{10}H_6{\cdot}OH,$$

obtained in light yellow plates after a week, was crystallised from benzene and light petroleum in pale yellow, prismatic crystals melting at 117·5° (Found: N = 10·28. $C_{18}H_{14}ON_2$ requires N = 10·22 per cent.). It is noteworthy that the saturation of the chromophore by hydrogen cyanide has not in this instance destroyed the colour of the substance.

o-*Nitrophenylamino-2-hydroxy-α-naphthylacetonitrile*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH(CN){\cdot}C_{10}H_6{\cdot}OH.$$

—After ten days in anhydrous hydrogen cyanide, the red, crystalline *ortho*-nitrated azomethine compound was replaced by yellow, glistening leaflets, which separated from benzene in pale yellow plates melting and decomposing at 153° (Found: N = 13·2. $C_{18}H_{13}O_3N_3$ requires N = 13·16 per cent.).

m-*Nitrophenylamino-2-hydroxy-α-naphthylacetonitrile*.—The addition of hydrogen cyanide was complete after ten days; the product crystallised from benzene in pale yellow needles melting at 127·5° (*Found*: N = 13·28 *per cent.*).

p-*Nitrophenylamino-2-hydroxy-α-naphthylacetonitrile*.—2-Hydroxy-α-naphthylidene-*p*-nitroaniline reacted with extreme slowness; it was suspended in ether and agitated daily with excess of anhydrous hydrogen cyanide for a period of three weeks, when the product had assumed a brownish-orange tint. This material was washed with water and extracted with benzene to remove any unaltered azomethine; the residue, when crystallised from alcohol, separated in orange-brown plates melting at 242° (Found: N = 13·42 per cent.).

II. *Azomethine Derivatives from 4-Hydroxy-α-naphthaldehyde.*

The reagents were heated under reflux for one to six hours in the minimum amount of alcohol required for solution. The products were not so readily crystallisable from alcohol as their isomerides from 2-hydroxy-α-naphthaldehyde. The *ortho*-compound, the most soluble of the series, was obtained after evaporating off the alcohol, and was crystallised from 50 per cent. acetic acid.

$HO{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO_2$.	Appearance.	M.p.	Requires N = 9·59 per cent.
4-Hydroxy-α-naphthylidene-o-nitroaniline	Reddish-brown powder.	150—151°	Found: N = 9·38.
4-Hydroxy-α-naphthylidene-m-nitroaniline	Reddish-brown powder.	188°	,, N = 9·66.
4-Hydroxy-α-naphthylidene-p-nitroaniline	Dark crimson, granular powder.	238°	,, N = 9·75.

Weighed quantities (0·02 to 0·05 gram) of the foregoing isomerides were placed in 5 c.c. of cold 10 per cent. aqueous sodium hydroxide. The *ortho*- and *meta*-nitro-compounds dissolved within four minutes to an orange solution. When left over-night, the dissolved azomethine derivatives underwent hydrolysis with liberation of the corresponding nitroaniline, the acidified filtrate giving 4-hydroxy-α-naphthaldehyde. 4-Hydroxy-α-naphthylidene-*p*-nitroaniline was far less soluble than its isomerides, and under the foregoing experimental conditions the greater part remained unchanged; the dissolved portion, which gave a yellow solution, underwent hydrolysis into its generators.

In alcoholic sodium hydroxide solution the *o*-, *m*-, and *p*-nitro-compounds dissolved, giving respectively transient deep orange, orange-yellow, and orange-red colorations which faded to pale

yellow tints. The *o*- and *m*-compounds gave intense yellow solutions with concentrated sulphuric acid, whereas the *p*-isomeride developed a deep orange coloration.

Addition of Hydrogen Cyanide to Azomethine Derivatives of 4-Hydroxy-α-naphthaldehyde.

Phenylamino-4-hydroxy-α-naphthylacetonitrile,
$C_6H_5{\cdot}NH{\cdot}CH(CN){\cdot}C_{10}H_6{\cdot}OH$,
produced as a brownish-yellow powder, crystallised from benzene in colourless, silky needles melting at 122·5° and becoming pink on exposure to air (Found: N = 10·24. $C_{18}H_{14}ON_2$ requires N = 10·22 per cent.).

o-*Nitrophenylamino-4-hydroxy-α-naphthylacetonitrile*,
$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH(CN){\cdot}C_{10}H_6{\cdot}OH$,
was obtained by leaving the *o*-nitro-azomethine compound in contact with hydrogen cyanide for ten days; it crystallised from benzene in pale brown needles melting at 167° (Found: N = 13·32. $C_{18}H_{13}O_3N_3$ requires N = 13·16 per cent.).

m-*Nitrophenylamino-4-hydroxy-α-naphthylacetonitrile* crystallised from benzene in very pale yellow, silky needles melting at 124—125° (Found: N = 13·22 per cent.).

p-*Nitrophenylamino-4-hydroxy-α-naphthylacetonitrile*.—4-Hydroxy-α-naphthylidene-*p*-nitroaniline was suspended in dry ether and agitated daily with excess of hydrogen cyanide over a period of four weeks, when the dark crimson colour had changed to deep orange. The product crystallised from benzene in yellowish-brown needles melting at 202° (Found: N = 13·30 per cent.).

III. *Nitration of 2-Hydroxy-α-naphthaldehyde and β-Naphthacoumarin.*

Nitro-2-hydroxy-α-naphthaldehyde, $NO_2{\cdot}C_{10}H_5(OH){\cdot}CHO$, was produced by adding 2 c.c. of nitric acid (d = 1·52) diluted with 3 c.c. of glacial acetic acid to 5 grams of 2-hydroxy-α-naphthaldehyde dissolved in 100 c.c. of the same solvent, the solution being subsequently heated at 100°. The nitro-derivative crystallised on cooling, and more was obtained on diluting with ice-water.

After crystallisation from benzene or aqueous alcohol, the nitro-aldehyde separated in pale yellow needles melting at 186—187° (Found: N = 6·49. $C_{11}H_7O_4N$ requires N = 6·45 per cent.).

This nitro-2-hydroxy-α-naphthaldehyde gave a sparingly soluble, orange-yellow *sodium* salt, and the *azomethine* derivative, $HO{\cdot}C_{10}H_5(NO_2){\cdot}CH{:}N{\cdot}C_6H_5$, with hot alcoholic aniline; the latter

product separating in well-defined, orange-red needles melting at 252—253° (Found: N = 9·71. $C_{17}H_{12}O_3N_2$ requires N = 9·59 per cent.). This azomethine compound was insoluble in cold and sparingly soluble in hot aqueous sodium hydroxide, and dissolved to a red solution in alcoholic soda.

Nitro-β-naphthacoumarin, $NO_2{\cdot}C_{10}H_5{<}^{O\text{———}}_{CH:CH}{>}CO$.—β-Naphthacoumarin, obtained in a 60 per cent. yield by heating equal parts of 2-hydroxy-α-naphthaldehyde and anhydrous sodium acetate with 50 parts of acetic anhydride (95 per cent.) in the rotating autoclave at 180° for three hours (pressure = 3 atm.), was crystallised from 50 per cent. acetic acid. Nitration was effected with two parts of nitric acid (d = 1·42) added to one part of naphthacoumarin in ten parts of glacial acetic acid. The solution set to a pale yellow mass, probably consisting of β-naphthacoumarin nitrate. Concentrated sulphuric acid was added until this substance entirely redissolved, when the solution was heated at 100° for two hours and poured on to ice. The nitration product crystallised from pyridine in bright yellow needles melting at 242° (Found: N = 6·09. $C_{13}H_7O_4N$ requires N = 5·81 per cent.).

The reduction of the foregoing nitro-compounds led to the production of somewhat oxidisable bases; the amino-β-naphthacoumarin, m. p. 180—182°, furnished acetyl, benzylidene, and azo-β-naphthol derivatives.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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Edgbaston. [*Received, December 14th,* 1921.]

II.—*The Overvoltage of the Mercury Cathode.*

By Edgar Newbery.

In a recent communication by Dunnill (*T.*, *1921*, **119**, *1081*), a careful and detailed description is given of the interesting behaviour of a mercury cathode. Unfortunately, the range of current density and the time employed were so limited that many important phenomena were overlooked. Only one of the three overvoltages

of mercury was observed, and although the small variations of this one value under slight changes of conditions were exhaustively studied, the much greater changes produced by extreme conditions were not obtained. Some of the results recorded differ materially from those obtained by the present author, and certain far-reaching conclusions were drawn which seem scarcely justified by the limited range of observations. With the view of explaining these discrepancies and testing these conclusions, the following work was undertaken. The conditions were made as far as possible identical with those of Dunnill's work, but were considerably extended in many directions, in order to obtain a fuller insight into the whole problem.

EXPERIMENTAL.

A glass vessel was taken having a cross section of approximately 10 sq. cm., and carefully purified mercury poured in to a depth of 1·5 cm., contact being made by a platinum wire sealed into the end of a glass tube and dipping to the bottom of the mercury. The anode consisted of a stout platinum wire, 1 cm. long, sealed into another glass tube and supported at varying distances (usually about 1 cm.) from the mercury surface. It was found that the position of the anode had little or no effect on the overvoltage, although the diameter of the ring free from visible bubbles was greatly affected by this motion.

The electrolyte was *N*-sulphuric acid, and a mercurous sulphate–mercury electrode in acid of the same strength was used as reference electrode. The jet of this electrode vessel (1 mm. in diameter) could be adjusted to any position with regard to the surface of the mercury, and it was soon found that important data as to the effect of change of position of this jet had been omitted from Dunnill's description. In his work, the jet is described as just touching the mercury surface immediately below the anode. In such a position it naturally interferes with the lines of flow of the current, but this may be a matter of little importance. Of much greater importance is the fact that there is a remarkably steep potential gradient in the immediate neighbourhood of the mercury surface during the passage of the current and the motion of the electrode jet through one millimetre in a *vertical* direction may alter the measured potential by more than one hundred millivolts. Depressing the jet 1 cm. under the mercury surface may change this potential by nearly one volt. Again, if the jet actually touches the metal, a new metal–electrolyte surface is introduced, and it is by no means certain that the metal thus imprisoned is in the same condition or has the same single potential as the surrounding metal. In addition to all this, the

tendency for gas bubbles to collect in the capillary is very marked, due to the imprisonment of metal saturated with hydride or supersaturated with hydrogen. The metallic solution, when thus released from the severe electric strain of the surrounding medium, at once liberates its hydrogen in the capillary tube, and a new metal-gas surface is formed having its own single potential, which duly appears among the factors present in the resultant measurements. It is evident, therefore, that the expedient of allowing the electrode jet to touch the mercury surface is a most dangerous one, and results thus obtained must be treated with the greatest caution.

In the experiments here described, the electrode jet (unless stated to the contrary) was supported about one millimetre above the mercury surface. When a commutator is used, the position of the jet *in the electrolyte* and the relative position of the leading-in wire to the mercury cathode have no effect on the measurements, whereas both these factors affect the results obtained without a commutator. Such factors have nothing to do with true overvoltage, and their presence therefore indicates a considerable error in the resultant measurements.

The following table illustrates the variation in measurements due to the position of the jet from the standard electrode with respect to the mercury surface. The current was 36 milliamperes and the commutator speed 1500 revs. per minute.

	10 mm. *above.*	1 mm. *above.*	*0.*	1 mm. *below.*	10 mm. *below.*
With commutator	0·40	0·40	0·40	0·37	0·18
Without commutator ...	0·70	0·67	0·58	0·41	0·08

The mercury in this case had been previously subjected to a high current density, but had been kept for forty-eight hours before the above readings were taken. In order to obtain the high values (which were the only ones observed by Dunnill), this mercury was treated with a current of 68 milliamperes for half an hour, when the expected jump of potential occurred and the above set of observations was repeated. Current and commutator speed as before.

Jet	10 mm. above.	1 mm. above.	0.	1 mm. below.	10 mm. below.
With commutator	0·81	0·81	0·81	0·80	0·56
Without commutator ...	1·13	1·10	1·07	0·98	0·45
Current increased to 68 milliamperes.					
With commutator	0·82	0·82	0·82	0·80	0·50
Without commutator ...	1·28	1·20	1·09	1·03	0·60

These figures illustrate very clearly how at least one source of serious error is eliminated by the use of a commutator, namely,

that due to change of position of the electrode jet in the electrolyte. When the jet is thrust far down into the mercury, the standard electrode practically becomes an independent cell, the negative electrode being formed by the surface of the mercury which enters the jet. This mercury is in contact with an unsaturated solution of mercurous sulphate, and is therefore of uncertain potential. Also, the position of the platinum connexion to the battery materially affects this potential, which is consequently very variable and of little theoretical interest. The steep potential gradient at the surface of the mercury cathode disappears the instant the current is interrupted, and this fact supplies one of many proofs which could be given of the existence of a gas film of high resistance on the surface.

All the above figures are averages of four complete sets of readings.

Effect of Commutator Velocity.

This has been discussed in detail in a communication sent to the *Journal of the American Chemical Society* early in August last, but the mercury electrode was not among those chosen. The figures given by Dunnill indicate a curve (overvoltage–commutator speed) so much steeper than any obtained with other electrodes that one is forced to the conclusion either that the rate of decomposition of the mercury overvoltage compounds is enormously greater than those of other metals, or that these figures are seriously affected by a mechanical defect in the commutator used.

In order to settle this point, a very careful and extended series of observations was taken (about 200 readings in all), the same current densities being used as those given by Dunnill, namely, 36 and 68 milliamperes per 10 sq. cm.

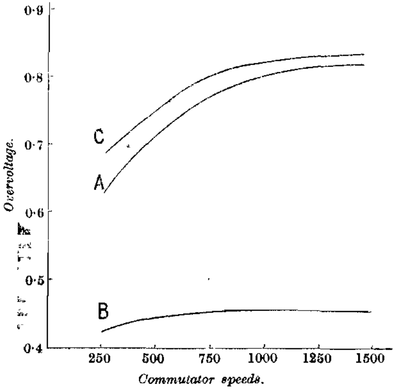
The commutator was 1·5 inches in diameter, having only two sections, and these were separated by ivory plugs ⅛ inch thick. It was constructed with a solid steel flywheel 6 inches in diameter and ⅝ inch thick on the same shaft, which ensured steady running, and was driven by a 200 volt motor with a rheostat in series. The rheostat was carefully calibrated to give speeds of from 250 to 1500 revs. per minute, and these speeds were checked from time to time during the course of the work. Before use, special care was taken to ensure that when the centre brush was on the ivory plug no current could pass in either direction. As will be seen later, it appears probable that neglect of this precaution has led to the abnormal results obtained by Dunnill.

Two sets of results were obtained at a current of 36 milliamperes, one with the mercury in the high and the other in the low over-

voltage condition, these conditions being quite easily obtained at any time, but not always easy to maintain. The following table gives the averages from about twenty sets of readings, current density being given in milliamperes per 10 sq. cm., and commutator speed in revolutions per minute.

			Commutator speeds.					
	Current.	Direct.	1500	1250	1000	750	500	250
A.	36	1·08	0·82	0·815	0·80	0·77	0·71	0·62
B.	36	0·83	0·45	0·45	0·45	0·445	0·44	0·42
C.	38	1·15	0·835	0·83	0·82	0·80	0·75	0·68

FIG. 1.



The curves in Fig. 1 illustrate these results graphically. It is evident that at the highest speed used the curves have already approached very near to a maximum, and extrapolation to infinite speed will give values not far removed from those observed at 1500 revs. per minute. In fact, curve *A* reaches 0·825 volt, curve *B* 0·45 volt, and curve *C* 0·84 volt when this extrapolation is carried out—values which are widely different from those obtained by the "direct" method.

On comparing these results with those of Dunnill, it will be observed that although his lowest commutator speed is identical with the highest here used, he obtains rises of 0·1 to 0·2 volt. It

appears highly probable, therefore, that his results have been vitiated by a defective commutator. If a perfectly clean break is not made from the main circuit before the potentiometer circuit is connected, some fraction of the main current is "dragged over" and greatly affects the potentiometer readings.*

These curves are of interest in that they show, not only the great instability of the compounds responsible for the high overvoltage of mercury, but also (curve *B*) the comparative stability of the compound producing the lower overvoltage.

Effect of Time.

The whole of Dunnill's work seems to have been done with mercury in the high overvoltage condition. This condition is usually, but not always, shown by pure fresh mercury electrodes, and is the stable state at low current densities. Since the highest current density he used was 7·8 milliamperes per sq. cm. and this only for a short time, he did not have an opportunity of observing the remarkable time effects previously described by the present author (*loc. cit.*). The following table shows the effect of time with low current density on the total back *E.M.F.* of mercury which had been kept for twenty-four hours in contact with the electrolyte but with no current flowing.

Area of cathode 10 sq. cm.; current 68 milliamperes; no commutator used.

Time in mins.	1	2	3	4	5	10	15	20	25	30	40	50	60
Back *E.M.F.*	0·78	0·79	0·79	0·80	0·80	0·81	0·82	0·83	0·86	1·15	1·20	1·23	1·24

After an interval of one hour with no current flowing, the same cathode was used at the same current density, but with a commutator speed of 1500 revs. per minute. The results were as follows:

Time in mins.	1	2	3	4	5	10	15	20	25	30	40	50	60
Overvoltage	0·67	0·74	0·77	0·79	0·80	0·83	0·84	0·85	0·85	0·85	0·85	0·85	0·85

These results are illustrated graphically in Fig. 2. It is evident that curve *B* is really a repetition of the latter part of curve *A* with the disturbing influence of transfer resistance removed.

The position and steepness of the rapidly rising portion of the curve are chiefly determined by the previous history of the electrode.

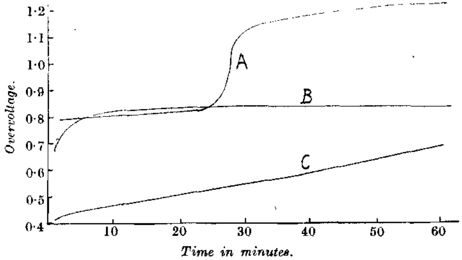
* The present author on one occasion wasted three days' work obtaining anomalous and irreproducible results before locating this source of trouble—in this case a single fine strand of wire from the brush disarranged by an unauthorised person rotating the commutator backwards.

Mercury which has been kept in contact with the electrolyte for some hours acquires an overvoltage of about 0·4 volt, and both the time required to change this value and the flattening of the rapidly rising portion of the curve are increased by long keeping. An illustration of an extreme case of this kind is seen in curve *C*, which was obtained under the same conditions as curve *B*, except that the cathode had been kept undisturbed for a week.

As might be expected, the time effect occurs more rapidly when a commutator is not used.

At high current densities, the change to low values occurs very rapidly. A cathode was showing a back *E.M.F.* of nearly 2 volts with a current density of 68 milliamperes when the current was

FIG. 2.



suddenly increased to 1000 milliamperes. In three minutes the back *E.M.F.* had fallen to 0·55 volt measured without a commutator and — 0·02 volt with a commutator. This rapid fall of overvoltage sometimes occurs after the application of a high current density even although the current has been greatly reduced in the meantime —a peculiar type of delayed action.

An interesting time effect is observed, not only with mercury electrodes, but also with nearly all metals, when the commutator velocity is varied. At high speeds there is a general tendency for the measured overvoltage to increase with time up to a definite maximum. At low speeds there is a similar tendency to decrease with time to a somewhat less definite minimum. If the maximum has been attained at a high speed and the commutator velocity is suddenly reduced, the measured overvoltage remains at its high value for an appreciable time and then falls gradually. This experiment may be carried to extremes by short-circuiting the

commutator for some time, which is equivalent to running it at an infinite speed, and removing the short-circuiting plug the instant before taking a reading. Values obtained in this way agree very well with those obtained by extrapolation of the overvoltage–commutator speed curves, and thus afford additional evidence for the trustworthiness of those values.

Effect of Current Density.

The very limited range of current density used by Durnill (11 to 78 milliamperes per 10 sq. cm.) gives a most unsatisfactory impression of the real effect of current density. In the work here described, an attempt was made to determine the effect of current density on mercury in both the high and very low (zero) overvoltage states. The latter is quite easy, but the former can only be done by very rapid working at the higher current densities owing to the great tendency of the electrode to change suddenly to the latter condition. By starting with an unused electrode and working at high speed, two complete series were obtained, both without and with a commutator. The values with the commutator agreed within 0·01 volt, whilst those without the commutator varied by 0·08 volt at the same current densities. Within thirty seconds after completing these series, the expected overvoltage fall occurred, although the current density was low at the moment. Two further series were then taken and are shown in column *B* in the following table. Column *A* shows the average values obtained in the first series. Current density is given in milliamperes per 10 sq. cm. Commutator speed 1500 revs. per minute.

Current Density.	With Commutator.		Without Commutator.	
	A.	*B*.	*A*.	*B*.
20	0·75	0·08	1·01	0·49
40	0·76	0·06	1·04	0·54
100	0·70	0·05	1·12	0·58
200	0·65	0·03	1·16	0·66
400	0·61	0·03	1·25	0·77
1000	0·57	0·03	1·42	1·03
2000	0·56	0·01		

The Three Overvoltages of Mercury.

From the work described, it is evident that mercury shows three fairly definite overvoltages—high (0·8 volt or more), low (0·4 volt approximately), and zero—corresponding with the bivalent, univalent, and zero-valent (no compound formed) states respectively. The first state is produced by, and is permanent at, low current densities and is generally shown by fresh mercury. The second

state is shown by mercury which has been kept for some time in contact with dilute acid, and appears to be unstable when current is flowing. It may be due to the formation of traces of mercurous salt adsorbed on the mercury surface and also carried into the body of the mercury by movements due to change of surface tension. This salt on decomposing would tend to give the hydride corresponding with univalent mercury, and therefore the lower overvoltage. The third state is permanent at high current densities, and when once acquired takes a considerable time for its removal. Its sudden appearance is accompanied by an equally sudden change in the size of the bubbles of gas liberated, from large to very small.

A Proposed Addition to the Previous Theory of Overvoltage.

The author has felt for a long time that his attempted explanations of the remarkable fall of overvoltage and of transfer resistance at high current densities have been very unsatisfactory. The present work has suggested another idea which not only appears much more reasonable at first sight, but also affords an explanation of the change of size of the gas bubbles and of the effect of stirring the electrolyte, which was quite inexplicable on the basis of the older theory alone.

At low current densities, the ions in the solution in the neighbourhood of the electrodes are at a distance from each other which is large compared with their own dimensions. At very high current densities this condition no longer holds, and the ions close to the electrode surface are packed so closely that an electron shot out from the electrode into an ion within range may travel with such velocity and produce such disturbance within the atom thus struck that the electron on the opposite side of the atom becomes loose enough to be seized by another ion close to the first ion but further away from the electrode. At extreme current densities the electrical tension near the electrodes is very high and this action will therefore become more general and more extended into the electrolyte. But this action involves the discharge of ions at a distance from the electrode. The tendency to the formation of a gas film and the production of high pressures will therefore be greatly reduced, and hence transfer resistance falls. At the same time, the reduction of the pressure will allow of the decomposition of the overvoltage compounds without inducing their re-formation and the overvoltage will therefore fall. The extremely minute bubbles seen under these conditions are a natural consequence of this discharge in the electrolyte, and the high degree of ionisation of the escaping gas (T., 1914, **105**, 2429) also follows.

Rapid stirring of the electrolyte at high current densities will tend to disturb the packing of the ions along the lines of force and will therefore lessen the distance discharge, thus producing a rise of overvoltage. At low current densities similar stirring will tend to remove the obstructing gas film, thus producing a fall of overvoltage. Both these phenomena were observed by the author in 1913, but until now he was able to offer no adequate explanation of them. The idea of chemical action at a distance from the electrode is not new, and has been applied in the electrolytic manufacture of white lead, but in this case the ions themselves are considered to be so closely packed that they form in one sense a conducting plate carrying the current from the electrode out into the electrolyte.

Conclusions.

It is evident from the work described that Dunnill's conclusion that "the direct method gives more accurate results" cannot be upheld, if the term "overvoltage" is to be confined to its legitimate object—the reversible portion of the total back electromotive force of an electrode. The commutator method is certainly liable to an error due to the very rapid decomposition of the overvoltage compounds, but this error is trifling compared with the very large effects produced by transfer resistance. Furthermore, this small error may be completely eliminated by the simple expedient of extrapolation to infinite commutator speed.

The statement on p. 1087 that "it would be difficult to give a direct proof of the presence of this film" (of gas on the electrode) is hard to understand. So far as the author is aware, this has never before been questioned, and is the usual text-book explanation of the phenomena of polarisation in a simple cell. The appearance of visible gas bubbles is in itself a direct proof of the supersaturation of the electrode surface with gas. Any denial of the existence of a gas film would introduce insuperable difficulties in explaining the simple phenomena of polarisation, gas electrodes, etc.

The surface tension phenomena described by Dunnill are interesting but appear to have no very direct connexion with the overvoltage of the cathode, as similar values are obtained whether the ring is present or not. The sudden appearance of the ring during an experiment coincides with no marked change of overvoltage, and the size of the ring is dependent on the position and shape of the anode. A small point not mentioned by Dunnill is that, although the mercury surface inside the ring appears to be travelling outwards, the small gas bubbles are often observed travelling from the walls of the containing vessel inwards towards the ring. In

conclusion, it appears highly probable that Dunnill's unsatisfactory results with a commutator are due to a defective apparatus, but his reasoning is also influenced by two questionable statements at the commencement of his paper—the first, that the surface of metallic mercury can be reproduced exactly, is open to serious doubt, whilst the second, that the properties of the surface are unchanged during the passage of the current, is disproved both by his own work and by the experiments here described.

Summary.

1. The overvoltage and the direct potential difference of a mercury cathode have been measured under wide variations of current density, time, commutator speed, etc.

2. Although the rate of decomposition of the overvoltage hydrides of mercury is high, a very close approximation to the true overvoltage is obtained when the commutator speed is not less than 1500 revs. per minute, and an exact estimate may be made by extrapolation to infinite speed.

3. No approximation to true overvoltage can be obtained without the use of a commutator.

4. Mercury shows three distinct overvoltages corresponding with the bivalent, univalent, and non-valent conditions. Directions are given whereby any one of these conditions may be obtained at will.

5. An extension of the previous theory of overvoltage is suggested which will account for the lowering of overvoltage and transfer resistance at high current densities, the diminished size of the gas bubbles under similar conditions, and the variable effect of stirring the electrolyte at different current densities.

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III.—*The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. Part III. The Action of Driers.*

By Samuel Coffey.

A method having been devised for obtaining the true oxygen absorption values of drying oils (T., 1921, **119**, 1152), it was determined to employ it in an attempt to elucidate the action of driers.

The rate of oxidation of linseed oil is affected by heat and sunlight and further by certain metals and their salts, which are known as "driers" or "siccatives." Fokin (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 609) suggested that their action was catalytic* because

(*a*) there appeared to be no stoicheiometric relation between the qnantity of drier and the amount of oxygen absorbed, and

(*b*) the reaction curve appeared to be logarithmic, of the form

$$k = \frac{m}{t_1} + \frac{1}{t_2} \log_e \frac{a}{a - x},$$

where t_1 is the period of induction where absorption is proportional to time. Also t_1 is diminished by a large amount of drier; hence he suggested that this stage corresponds with molecular autoxidation and that probably molecular and atomic oxidation proceed simultaneously. Later (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276) he suggested that the oxidation of linseed oil was a process of molecular autoxidation accompanied by a decomposition of the products of the reaction into volatile and complex substances. He also supposed that the absorption could be carried out without the formation of volatile products if metallic oxides were present, but, as will be shown later, this is erroneous. He considered that his results showed that the oxidation in films and in solution in the presence of driers proceeded by the same two stages, namely,

$$x_1 = k_1 t_1 \text{ for the induction period.}$$

$$\frac{dx_2}{dt_2} = k_2 (a - x_2) \text{ after the induction period.}$$

According to Fokin, Ostwald's formula for autoxidation does not hold, and also the reaction is probably one of autoxidation, the function of the drier being represented by

$$AO_2 + \underset{\text{(Oil.)}}{B} = AO + BO,$$

where A denotes a metal.

Ingle also (*J. Soc. Chem. Ind.*, 1917, **36**, 379) has put forward a catalytic hypothesis according to which the basic (lead) oxide first hydrolyses the oil and then acts catalytically by forming an unstable peroxide. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658; 1911, **43**, 1509) found that linoxyn was unsaturated, that the correct *apparent* oxygen absorption value was 15—16 per cent., and that, with a cobalt drier, setting took place when the absorption was 12 per cent. He found that the equation for the reaction approximated to the empirical equation

$$\frac{dx}{dt} = k (A - x)(B + x),$$

* Mulder (1867) assumed driers to be catalysts.

where A is the total amount of oxygen absorbed and B is a constant. Thus Fokin and Orloff consider that the action of driers is catalytic and that the apparent oxidation curve approximates after a time to that of a unimolecular reaction.

If the action of driers is purely catalytic, that is, if they act in no other way than as oxygen carriers, then it can be assumed that the true oxygen absorption for a given oil is a constant quantity, no matter what the drier may be and no matter what its concentration. Unfortunately, apparently no data exist on this point save, perhaps, those of Lippert (*Z. angew. Chem.*, 1898, **11**, 412, 431), which show that the maximum *apparent* oxygen absorption gradually decreases as the amount of drier increases. As all this work, however, deals with *apparent* oxygen values, the figures are of little use.*

According to Fokin, the following metals and their salts act as driers, the most active being placed first :—

Co, Mn, Cr, Ni, Fe, Pt, Pd, Pb, Ca, Ba, Bi, Hg, U, Cu, Zn; the metals following lead are only " weak " driers.

In this investigation, litharge, red lead, manganese borate, lead acetate and cobalt oxide were taken as being a fair representation of the numerous driers used commercially.

EXPERIMENTAL.

The same linseed oil was used as in the determination of the true oxygen absorption of oil alone, and the apparatus was that fully described in Part I of this research (*loc. cit.*). The true oxygen absorption of the oil was 28·7 per cent., and its iodine value 184·1.

The drier in each case was ground as finely as possible.

A known amount of oil was placed on a filter-paper in the way already described (*loc. cit.*, p. 1154) and the drier was deposited on each surface of the oil film in a thin uniform layer by allowing it to fall on the paper in a fine cloud from a height of about 30 cm. Care was taken to cover the surface of the oil as completely as possible, but, on the other hand, a relatively thick film of drier was avoided. The prepared paper was quickly placed in the absorption apparatus, which was then flooded with hydrogen, heated to the desired temperature, and finally flooded with oxygen. The subsequent procedure was exactly that described for the determination of the oxygen absorption of the oil in the absence of a drier (*loc. cit.*). The results obtained with the above driers are given in Table I.

* Fahrion (*Chem. Zeit.*, 1904, **28**, 1196) overlooks this fact in his discussion of the subject.

TABLE I.

True oxygen absorption in the presence of driers.

Drier.	Weight of oil. Gram.	Oxygen absorption Per cent.	
Cobalt oxide	0·5515	24·0	
,,	0·6988	26·4	
,,	0·9356	27·3	
,,	0·5879	27·4	
Litharge	0·5030	17·9	
,,	0·6245	17.1	Mean 17·1
,,	0·7738	17·1	
,,	0·5670	17·0	
Manganese borate	0·6537	22·2	
,,	0·6740	23·6	
,,	0·6430	23·0	

Drier.	Weight of oil. Gram.	Oxygen absorption. Per cent.	
Red lead	0·5648	17·7	
,,	0·5964	17·4	Mean 17.1
,,	0·7360	17·1	
,,	0·6120	16·8	
Lead acetate	0·7306	23·9	
,,	0·5841	26·4	
,,	0·6382	21·8	
,,	0·5630	26·0	

Cobalt Oxide.—The black " chemically pure " oxide was ignited before use. The drier was very dense, and some difficulty was experienced in obtaining a good distribution without using a relatively thick layer. The results are all lower than the true oxygen absorption for the oil alone, but no constancy is obtained. This may be due to the inferior distribution.

Litharge.—This was a good sample free from metal or peroxide. It was extremely fine and was exceptionally easily deposited on the oil surface. The distribution was particularly good, and as far as could be seen was all that could be desired. These results are again lower than those obtained without a drier, being about 0·6 of this value and approaching the recognised apparent oxygen value for the oil alone, namely, 18 per cent., but they differ from those obtained with cobalt oxide in that, with the exception of the first value, they are quite constant at 17·1 per cent.

Manganese Borate.—This was a sample of the commercial article Although thoroughly ground, it was extremely difficult to distribute it satisfactorily. The results are again lower than those obtained without the drier.

Red Lead.—This drier, like the monoxide, was extremely fine, and the distribution excellent, being both thin and uniform. The deposits on the papers after oxidation were still bright red. These values are again much lower than those obtained without a drier, and are fairly constant at 17·1 per cent., the same value as for litharge.

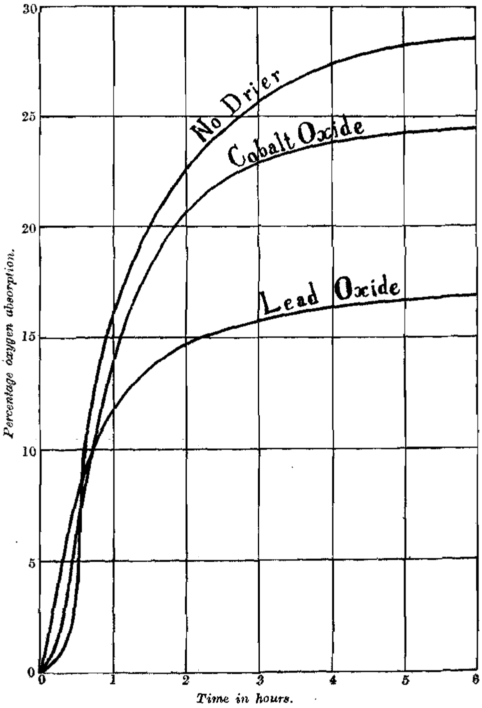
Lead Acetate.—The recrystallised hydrate, $Pb(C_2H_3O_2)_2,3H_2O$, was used. In this case it was very difficult to secure a good distribution, and the results therefore are not trustworthy. They show, however, that the amount of oxidation in the presence of lead acetate is smaller than that in the absence of the drier.

The Oxidation Curves.

Fig. 1 shows the curves obtained for the oil alone and for the oil with cobalt oxide and with litharge or red lead as the drier. In the case of the lead oxides the reaction curves are coincident over

FIG. 1.

Oxidation curves for linseed oil with and without a drier.



their whole length. In the presence of the drier there is practically no period of induction, but the time required for complete oxidation is the same as that required for the oil alone without the induction period. In the presence of a drier, therefore, only the induction period is shortened, the rate of the main oxidation being unaltered. Since, however, the induction period for oil alone is extremely large at the ordinary temperature, the "accelerating" effect of a drier becomes explicable.

The method of experiment in this investigation might possibly be criticised on the ground that the low oxygen absorption in the presence of driers may be due to the compound forming a protective layer on the oil surface, thereby preventing its oxidation. This objection appears to be negatived, however, by the following facts: (*a*) the values for the oxides of lead are quite constant, (*b*) complete oxidation takes place, and (*c*) the reaction curves, although indicating a smaller oxygen absorption, do not run parallel to the curve for oil alone. Also, as will be seen from Fig. 1, the curves deviate even more than the curve for oil alone from the simple logarithmic curve suggested by Fokin and others.

Discussion of Results and Conclusions.

From the foregoing results it is evident that the presence of a drier modifies the course of the oxidation of linseed oil, because in every case the oxygen absorption recorded is lower than that observed when no drier is present, and the reaction curves are different. Analogous results were obtained by Morrell (T., 1918, **113**, 111) in his investigation of the oxidation of the cerium salts of linolenic and α-elæostearic acids. According to these results, α-elæostearic acid, an isomeride of linolic acid, in the presence of a cerium drier, absorbs only one molecule of oxygen and not two. The oxidation of linolenic acid, however, appears to be far more complex. The acid used was doubtless a mixture of the α- and β-isomerides, and, as has been shown in Part II of this work, this would introduce undesirable complications (T., 1921, **119**, 1408). His results show, however, that in all probability the oxidation of cerium linolenate is not so extensive as that of free linolenic acid. If in the case of linolic acid with lead oxide as a drier the oxygen absorption also amounts to one molecule, then this accounts for 5·54 per cent. of the absorption of oxygen by the oil employed in these experiments (compare T., 1921, **119**, 1411). This leaves 11·56 per cent. for the α-linolenic acid, which means that, in the presence of this particular drier, the acid absorbs exactly six atoms of oxygen. This supposition has received no direct experimental

confirmation, but in the light of the results given in Part II and in Morrell's work it would seem to be very probable.

It is also interesting to note that in the presence of a drier the amount of carbon dioxide evolved during the oxidation is approximately the same as for the oil alone. Owing to the basic properties of the drier, however, an accurate estimation of the volatile products was not possible. In the presence of driers (PbO) no trace of hydrogen peroxide could be detected.

In the light of the above evidence, although the drier may remain unchanged—an assumption that has yet to be verified—it does not act as a catalyst in the strictest sense, because it obviously changes the course of the reaction. Thus the large amount of work which has been carried out in the presence of driers and based upon the assumption that the latter are true catalysts, is not comparable with that done on oil alone.

The author takes this opportunity to express his great indebtedness to Professor F. S. Kipping, F.R.S., in whose laboratory the experiments were carried out, for his constant advice during this work, and also to the Commissioners of the 1851 Exhibition for a scholarship which enabled him to complete the investigations.

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IV.—*Catechutannins. Part I. Paullinia Tannin.*

By Maximilian Nierenstein.

It has recently been suggested by Freudenberg (*Ber.*, 1920, **53**, [*B*], 1417; compare Löwe, *J. pr. Chem.*, 1868, [i], **105**, 33, 75; Etti, *Monatsh*, 1889, **10**, 467) that the catechutannins are amorphous dehydration products of catechin. As evidence in support of this view, Freudenberg quotes Kirmsse (*Arch. Pharm.*, 1898, **236**, 122), who, during the course of an investigation of guarana, a paste obtained from the seeds of *Paullinia cupana*, H. B. & K., was able to isolate a crystalline catechin in addition to amorphous guarana tannin.* A deduction based on this observation cannot

* For a summary of the literature of catechutannins in general, and of guarana and paullinia tannins in particular, see Perkin and Everest, "The Natural Organic Colouring Matters," 1918, and Dekker, "Die Gerbstoffe," *1913* respectively.

be taken seriously, since the manufacture of guarana involves a series of vigorous processes, including the roasting of the seeds (compare Planchon and Collin, "Les Drogues simple d'origine végétale," 1898, **2**, 576). It is therefore very probable that the catechin found by Kirmsse in guarana is a disintegration product of guarana tannin.

The results obtained by the author are in every respect opposed to Freudenberg's theory, since paullinia tannin is found to be a crystalline substance, consisting of one molecule of dextrose and two molecules of gambier-catechin * carboxylic acid. The latter acid is not identical with the synthetic gambier-catechin carboxylic acid previously described (*Annalen*, 1913, **396**, 194). As these two acids are probably isomerides, it is proposed, provisionally, *to employ the prefix* α *for the synthetic acid and* β *for the acid* occurring in paullinia tannin.

The present investigation shows that the two molecules of β-*gambier-catechin carboxylic acid* in paullinia tannin form a depside (compare Fischer, *Ber.*, 1913, **46**, 3253), since the methylo-derivative, prepared by the action of diazomethane on paullinia tannin, yields tetramethyl glucose on hydrolysis (compare T., 1921, **119**, 284). As paullinia tannin contains a free carboxyl group and when hydrolysed with emulsin yields both β-gambier-catechin carboxylic acid and dextrose, it becomes also evident that this tannin is a normal glucoside (compare Fischer and Strauss, *Ber.*, 1912, **45**, 2467) and not an acyl derivative of glucose, as assumed by Fischer in the case of gallotannin.

Our incomplete knowledge of gambier-catechin makes it impossible to discuss the constitutions of β-gambier-catechin carboxylic acid † and paullinia tannin, hence at present an empirical formula only is assigned to the latter :

$$C_{15}H_8O(OH)_5\cdot CO\cdot O\cdot \underset{}{\overset{O\cdot C_6H_{11}O_5}{\overset{|}{C}}}{}_{15}H_8O(OH)_3\cdot CO_2H$$

It should be noted that the methylo-derivative of paullinia tannin, on hydrolysis, yields, in addition to tetramethyl glucose, *penta-methoxy-* and *trimethoxy-β-gambier-catechin carboxylic acid.* The

* The catechin found by Kirmsse in guarana is obviously gambier-catechin, although he gives no melting point for his product (compare A. G. Perkin and Yoshitake, T., 1902, **81**, 1163, 1173). Freudenberg's suggestion ("Die Chemie der natürlichen Gerbstoffe," 1920) of the special name paullinia-catechin for this substance is consequently not required.

† The graphical formula previously assigned to α-gambier-catechin carboxylic acid (*loc. cit.*, p. 195) is withdrawn, as it was based on the catechin formula of Kostanecki and Lampe (*Ber.*, 1906, **39**, 4007), which has since become untenable (T., 1920, **117**, 973).

latter acid gives a pronounced green coloration with alcoholic ferric chloride, thus showing that in paullinia tannin the catechol nucleus in one molecule of β-gambier-catechin carboxylic acid is combined directly with the other molecule of β-gambier-catechin carboxylic acid and also with dextrose.

EXPERIMENTAL.

Preparation of Paullinia Tannin.

The seeds of *Paullinia cupana* are extracted in a Soxhlet apparatus with (1) ether and chloroform to remove chlorophyll and fats, and (2) ethyl acetate. The tannin is removed from the latter extract by shaking with a solution of sodium hydrogen carbonate saturated with carbon dioxide. The acidified aqueous solution is again extracted with ethyl acetate, the extract dried over anhydrous sodium sulphate, and the residue obtained on evaporation dissolved in hot water. The cold solution is shaken with 3 to 5 grams of fat-free caseinogen in order to remove any amorphous tannin (compare T., 1919, **115**, 1330). The filtrate, to which a few drops of chloroform are added, is allowed to stand in the cold. Crystallisation commences after three to four days, paullinia tannin separating in small needles. These are filtered and recrystallised several times from water, chloroform being added each time. The average yield from 500 grams of the seeds is 12 grams, which may be increased to 16 grams on concentrating the filtrates (Found *: C = 55·9, 56·3, 56·0; H = 4·6, 4·4, 4·5; CO_2H † = 5·7, 5·6, 5·3. $C_{37}H_{35}O_{18}{\cdot}CO_2H$ requires C = 56·2; H = 4·4; CO_2H = 5·5 per cent. Found : *M* in alcohol = 795, 820, 816, 843 ; *M* in water = 956, 872, 840, 836. Calc., *M* = 812).

Paullinia tannin crystallises from water in gray-coloured needles, which melt at 199—201°, carbon dioxide being evolved. At 130°, it loses two molecules of water of crystallisation (Found: H_2O = 4·2, 4·3. Calc., H_2O = 4·2 per cent.); the anhydrous product melts at 259—261°, with evolution of carbon dioxide and decomposition. The tannin is soluble in alcohol, ethyl acetate, or acetic acid, but not in any other organic solvent. Paullinia tannin gives all the typical colour tests of the catechutannins and

* Dried at 130°.

† By the method of Baumann and Kux (*Z. anal. Chem.*, 1893, **32**, 129). Preliminary experiments with phloroglucinolcarboxylic acid, protocatechuic and 2 : 3-dihydroxybenzoic acids gave good results by this method, which was, however, found not to be trustworthy in the case of gallic acid and pyrogallolcarboxylic acid.

is precipitated by gelatin * and alkaloids. The crystalline *sodium* and *potassium* salts are obtained by neutralisation of the tannin with the corresponding carbonates. They crystallise from water; they do not melt below 320° (Found: Na = 3·2, 2·9. Calc., Na = 2·7 per cent. Found: K = 6·1. Calc., K = 5·7 per cent.). The dextrose content of paullinia tannin is estimated in the same manner as in gallotannin (T., 1921, **119**, 279) (Found: dextrose = 21·6, 21·8, 22·3, 21·9. Calc., dextrose = 22·2 per cent.). The dextrosazone (m. p. and mixed m. p. 202—204°) was also prepared (Found: N = 15·9. Calc., N = 15·6 per cent.). Paullinia tannin gives the following optical data †: $[\alpha]_D^{20}$ − 74·4° (10 per cent. solution in water); $[\alpha]_D^{18}$ − 39·1° (8 per cent. solution in alcohol); $[\alpha]_D^{18}$ − 48·1° (6 per cent. solution in acetone); $[\alpha]_D^{20}$ − 56·8° (8 per cent. solution in pyridine). All solutions exhibit mutarotation, which is most evident in the case of the pyridine solution. The rotation falls from $[\alpha]_D^{20}$ − 56·8° to − 11·4° in sixteen minutes and to − 8·6° in forty minutes, when it becomes constant.

Action of Emulsin on Paullinia Tannin.

To a solution of 10 grams of paullinia tannin in 200 c.c. of water 0·3 gram of emulsin (from bitter almonds) in 75 c.c. of water, and 5 c.c. of chloroform are added. The solution, on keeping at 37° for eight days, deposits a mass of crystals which are filtered off. The filtrate, freed from unchanged paullinia tannin with the aid of lead acetate and hydrogen sulphide, contains dextrose, which is identified as the dextrosazone (m. p. and mixed m. p. 201—203°). The solid formed by the action of emulsin crystallises from water in small, pointed needles and is optically inactive *β-gambier-catechin carboxylic acid*, which melts at 252—253°, carbon dioxide being evolved (Found ‡: C = 57·3, 57·5; H = 4·8, 4·4. $C_{16}H_{14}O_8$ requires C = 57·5; H = 4·2 per cent.). The acid is soluble in alcohol, ethyl acetate, or acetic acid, but not in any other of the usual organic solvents. On heating an alcoholic solution of the acid with pyridine for several hours (compare T., 1916, **109**, 593), gambier-catechin is readily obtained. The latter, on crystallisation from distilled water, melts at 175—177°, which is the melting point

* Freudenberg's statement (*Ber.*, 1920, **53**, [*B*], 236) that gambier-catechin is precipitated by gelatin is not correct, as repeated observations in this laboratory have shown. His observation is also contrary to all previous data on this point (compare, for example, Procter, "Leather Industries Laboratory Book," 1908, p. 139).

† l = 4·4 for all optical observations given in this paper.

‡ Dried at 100° in a vacuum.

given by A. G. Perkin and Yoshitake (T., 1902, **81**, 1163) for gambier-catechin. This melting point is not depressed when the substance is mixed with authentic gambier-catechin (Found *: C = 62·0; H = 4·9. Calc., C = 62·1; H = 4·8 per cent.). The acetyl derivative was also prepared. It melted correctly at 124—125° and showed no depression when mixed with authentic penta-acetyl-gambier-catechin.

Diazomethane converts β-gambier-catechin-carboxylic acid into the corresponding *pentamethoxy methyl ester*, which crystallises from light petroleum in long needles, melting at 74° (Found †: C = 63·3; H = 6·5. $C_{22}H_{26}O_8$ requires C = 63·2; H = 6·2 per cent.). When oxidised with potassium permanganate in alkaline solution, veratric acid is obtained (m. p. and mixed m. p. 179—180°) (Found: C = 59·1; H = 5·8. Calc., C = 59·3; H = 5·5 per cent.). In this connexion it is interesting to note that the methyl ester of pentamethoxy-α-gambier-catechin carboxylic acid (m. p. 92°) previously described (*loc. cit.*) gives under similar conditions *m*-hemipinic acid and not veratric acid.

The inactive β-gambier-catechin carboxylic acid yields a crystalline *strychnine* salt, long, pointed needles from water, which melt at 222—223° (Found: N = 4·5. Calc., N = 4·2 per cent.). The *quinine* salt, however, was found to be the most suitable for the resolution of the acid. The two optically active forms are obtained on fractional crystallisation, the salt of the *d*-form being less soluble than that of the *l*-form. The free acids are obtained by decomposing the quinine salts with sodium hydroxide in the cold.

d-β-*Gambier-catechin carboxylic acid* crystallises from water in microscopic needles, which melt at 249—251°, carbon dioxide being evolved (Found ‡: C = 57·6; H = 4·5. Calc., C = 57·7; H = 4·2 per cent.). The rotatory power in water (5 per cent. solution) is $[\alpha]_D^{20°}$ + 12·6°; in alcohol (7 per cent. solution) $[\alpha]_D^{17°}$ + 17·6°.

l-β-*Gambier-catechin carboxylic acid* crystallises from water in fairly large needles, which melt at 258—261°, carbon dioxide being evolved (Found ‡: C = 57·3; H = 4·3. Calc., C = 57·5; H = 4·2 per cent.). The rotatory power in water (5 per cent. solution) is $[\alpha]_D^{18°}$ − 22·4°; in alcohol (6 per cent. solution) $[\alpha]_D^{17°}$ − 31·6°.

Methylated Paullinia Tannin.

The methylo-derivative is obtained in excellent yield by the action of diazomethane on an ethereal suspension of paullinia tannin. It crystallises from dilute alcohol or acetone in small needles, which melt at 126—127° [Found †: C = 60·2, 60·3, 60·1; H = 6·6, 6·5,

* Dried at 100°. † Dried in a vacuum over paraffin. ‡ Dried at 130°.

6·4; OMe = 43·2, 43·0, 43·1. $C_{38}H_{23}O_7(OMe)_{13}$ requires C = 60·5; H = 6·3; OMe = 43·1 per cent.]. It is soluble in all the usual reagents with the exception of water. The rotatory power in alcohol (5 per cent. solution) is $[\alpha]_D^{15^\circ}$ − 31·8°; in benzene (8 per cent. solution) $[\alpha]_D^{15^\circ}$ − 26·4°; in chloroform (6 per cent. solution) $[\alpha]_D^{15^\circ}$ − 37·7°; in *s*-tetrachloroethane (7 per cent. solution) $[\alpha]_D^{17^\circ}$ − 47·1°.

Hydrolysis of Methylated Paullinia Tannin.—Eight grams of the methylo-derivative are hydrolysed in a sealed tube with 100 c.c. of glacial acetic acid as described in the case of methylated gallotannin (T., 1921, **119**, 284). The semi-crystalline solid formed consists mainly of *trimethoxy-β-gambier-catechin carboxylic acid*, which crystallises from alcohol in small needles, melting at 174—175° (Found *: C = 60·5; H = 5·5. $C_{19}H_{20}O_8$ requires C = 60·6; H = 5·3 per cent.). On methylation with diazomethane, it is quantitatively converted into methyl pentamethoxy-β-gambier-catechin carboxylate (m. p. and mixed m. p. 74°). The acetic acid filtrate gives on addition of water a bulky precipitate, which consists mainly of *pentamethoxy-β-gambier-catechin carboxylic acid*. It crystallises from alcohol, acetic acid, or ethyl acetate in pointed needles which melt at 196—197° (Found *: C = 62·2; H = 6·3. $C_{21}H_{24}O_8$ requires C = 62·4; H = 6·0 per cent.). Diazomethane converts it quantitatively into the methyl ester (m. p. and mixed m. p. 74°).

The remaining filtrate contains tetramethyl glucose, which is isolated in exactly the same manner as used in the case of methylated gallotannin. It melts at 91—93°, and the melting point is not depressed by admixture with authentic tetramethyl α-glucose (Found: OMe = 52·2. Calc., OMe = 52·6 per cent.).

This investigation has, with many interruptions, been in progress since 1908, during which time the author has had the collaboration of Messrs. C. W. Spiers, M.Sc., and R. Barr, B.Sc., for which he wishes to thank them. He also wishes to acknowledge the help of the late K. C. R. Daniel, B.Sc. The author is also indebted to the Director of the Servico Sanitario of Manaos, North Brazil, for a liberal supply of material used in this investigation, and to the Colston Society of the University of Bristol for a grant in aid of this research.

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* Dried at 130°.

V.—*Researches on the Metallic Carbonyls.*

By Robert Ludwig Mond and Albert Edward Wallis.

Iond, Hirtz, and Cowap (T., 1910, **97**, 798) describe the methods f preparation and some of the properties of the metallic carbonyls. Ve have continued these researches, but owing to the great diffi- ulty with which these compounds are prepared, our knowledge of heir chemical and physical properties is still very incomplete. We esired, for instance, to study the compound $Mo(CO)_6$, but it equired two years to prepare 170 milligrams of this carbonyl, using he apparatus and methods described in the above paper.

The Composition of Molybdenum Carbonyl.

The analysis of this compound, as given by Mond, Hirtz, and 'owap, is "Found, CO = 0·0432 gram. Mo = 0·0279 gram. The ormula is therefore $Mo(CO)_6$."

The actual ratio Mo : CO given by the above analysis is 1 : 5·3. leference to the authors' notebook showed that they found 0·0249 ram of Mo, and not 0·0279 as published. This gives a molecular atio of 1 : 6·01.

It seemed desirable, however, to repeat the analysis of this arbonyl, and this we did by two different methods.

In the first analysis 40 mg. of the carbonyl were heated in a sealed ibe for ten hours at 240°, whereby the compound was completely ecomposed. The resulting gases were measured and analysed, nd the molybdenum remaining in the tube was dissolved out and stimated as lead molybdate (Found: Mo : CO = 1 : 5·20).

In the second analysis, 103 mg. of the resublimed carbonyl were ecomposed by bromine water. The evolved carbon monoxide 'as collected, measured, and analysed, and the molybdenum in olution estimated as lead molybdate (Found: 62·0 mg. CO and 1·3 mg. Mo). This gives a molecular ratio Mo : CO = 1 : 5·18.

These analyses suggest that the composition of molybdenum arbonyl is not represented by the formula $Mo(CO)_6$, and that the iolecule is very large, the constitution of which is probably $Io_5(CO)_{26}$. Molybdenum carbonyl is almost insoluble in benzene, lcohol, or other common solvents, so that its molecular weight annot be determined by the cryoscopic method.

Ruthenium Carbonyls.

The existence of a volatile compound of ruthenium and carbon monoxide was mentioned by Mond, Hirtz, and Cowap. It is obtained by heating the metal at 300° with carbon monoxide at 400 atmospheres. We have not obtained sufficient to determine its composition. This carbonyl is crystalline, and is soluble in benzene, but is insoluble in alcohol and in water.

Non-volatile Ruthenium Carbonyl.—Upon examining the contents of the retort after treating ruthenium with carbon monoxide for fifty hours at 250° and 350 atms., we found a quantity of chocolate-brown powder, which was insoluble in benzene and readily soluble in alcohol or water. The bulk of the powder was dissolved in alcohol, filtered from the unattacked ruthenium, and the solution evaporated in a current of hydrogen at 85°. The residue was then dried in a vacuum at 40°. The resulting brown, amorphous powder possessed all the characteristic properties of a metallic carbonyl.

The powder was analysed by heating it in a sealed tube at 400° for several hours, after which the gases in the tube were measured and analysed, and the deposited ruthenium metal was estimated: 64·8 mg. of the powder contained 42·1 mg. of Ru and 24·8 mg. of CO. This gives a molecular ratio Ru : CO = 1 : 2·14. The compound is therefore $Ru(CO)_2$.

This new metallic carbonyl differs from all others by being soluble in water and completely insoluble in benzene.

Iron Pentacarbonyl.

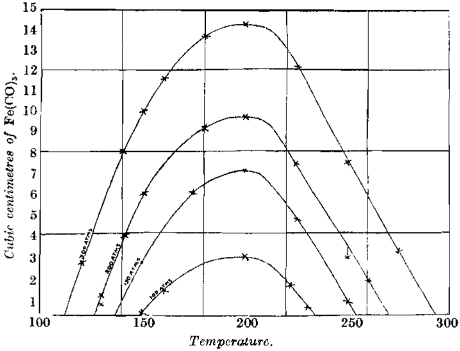
This compound was described in a paper by the late Drs. Ludwig Mond and Quincke (T., 1891, **59**, 604). It has been comparatively easy to prepare it in small quantities up to a few cubic centimetres, but, in spite of continuous efforts, it was found nearly impossible to obtain a reasonable yield, although we have undertaken a careful examination of the yield at different temperatures and pressures so as to obtain the best conditions for the preparation of this compound. The following pressure-temperature experiments were carried out in the high-pressure apparatus previously described (Mond, Hirtz, and Cowap, *loc. cit.*).

The retort used had a total capacity of 49·2 c.c., and into this were placed 30 grams of finely divided (pyrophoric) iron, which had been prepared by the reduction of ferric oxide by hydrogen at 450°. The iron was then allowed to react with carbon monoxide at the desired temperature and at constant pressure for two hours. The gases in

the retort were then rapidly passed through tubes cooled to − 20°, and the condensed iron pentacarbonyl was measured.

Iron pentacarbonyl, $Fe(CO)_5$.

Pressure-temperature experiments (100 *to* 300 *atmospheres*).



This process was repeated for each of the determinations given below :

100 atms.		150 atms.		200 atms.		300 atms.	
Temp.	C.c. of $Fe(CO)_5$.	Temp.	C.c. of $Fe(CO)_5$.	Temp.	C.c. of $Fe(CO)_5$.	Temp.	C.c. of $Fe(CO)_5$.
150°	0·20	150°	2·70	130°	0·70 (1·00)	120°	2·60
160	1·30	175	6·10	140	3·90	140	8·00
200	2·90	200	7·00	150	6·00	150	10·00
220	1·50	225	4·70	180	9·20	160	11·60
230	0·30	250	0·60	200	9·75	222	14·30
				225	7·50	235	12·20
				250	2·80	250	7·60
				260	1·60	275	3·30

We have plotted these results, and the curves show how rapidly the formation of the carbonyl diminishes above 200°. Up to this temperature, there is practically no conversion of carbon monoxide into carbon dioxide and carbon, but above it the rate of the reaction $2CO = CO_2 + C$ increases as the yield of carbonyl decreases.

Nickel Carbonyl and Oxygen.

Some attention has been directed to the varnish-like solid which Mond, Hirtz, and Cowap state to be a colloidal oxide of nickel

obtained by heating at 200° a mixture of nickel carbonyl vapour, air, and carbon monoxide. If moist carbon monoxide containing about 5 per cent. of nickel carbonyl vapour and sufficient air to oxidise the latter is passed through a tube at 200°, a golden-yellow deposit is obtained. As the deposit thickens, it becomes opaque and metallic in appearance. Repeated analysis of this substance showed that it is a colloidal basic carbonate of nickel of varying composition.

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VI.—*The Action of Nitric Oxide on the Metallic Carbonyls.*

By ROBERT LUDWIG MOND and ALBERT EDWARD WALLIS.

SINCE the discovery of the first of the metallic carbonyls by Mond, Langer, and Quincke (T., 1890, **57**, 749) up to the present time, many experiments have been made to induce the metallic carbonyls to enter into a chemical combination. Hitherto all these attempts have failed, complete decomposition of the carbonyl invariably resulting; and the absence of such compounds makes it increasingly difficult to form a satisfactory theory as to the molecular structure of these remarkable compounds.

Berthelot, who examined the action of numerous reagents on nickel carbonyl (*Compt. rend.*, 1891, **112**, 1347), states that when nitric oxide gas is mixed with nickel carbonyl vapour, or is passed into the liquid carbonyl, a blue compound of complex composition is obtained. We have endeavoured to ascertain the composition of this compound.

If a 1 per cent. solution of the carbonyl in chloroform or xylene is treated with nitric oxide gas at room temperature, it is coloured an intense blue. If, in the absence of air, the solution is then evaporated, a pale blue powder is obtained. This powder has an odour of almonds, is insoluble in water or other common solvent, and is immediately decomposed by dilute sulphuric acid with the evolution of oxides of nitrogen. From a stronger solution, or from pure nickel carbonyl, nitric oxide slowly deposits the blue compound. It may be filtered, washed with chloroform, and dried in a current of carbon dioxide at a temperature not above 60°.

If the temperature reaches 90°, the powder decomposes with brilliant incandescence.

The analysis of the compound was rendered very difficult by the fact that from very large amounts of carbonyl only a few centigrams of the blue powder could be obtained. In addition to this difficulty, nickel carbonyl is rapidly decomposed by the faintest trace of moisture, hydroxides or basic carbonates of nickel being produced.

The compound, or mixture of compounds, contained from 37 to 42 per cent. of nickel, 15 to 16 per cent. of nitrogen, and 10 to 15 per cent. of moisture. Even after repeated analysis we are unable to state definitely the composition of the compound, as we have never succeeded in obtaining it in a pure state. The behaviour of tbe blue compound towards reagents and tbe violence with which it decomposes at 90° in an atmosphere of inert gas suggest that it is a compound of nickel and nitric oxide, such as $Ni(NO)_2$, and that this dissociates at 90° witb subsequent violent reaction of the products. Sabatier and Senderens (*Compt. rend.*, 1892, **114**, 1429) observed that finely divided nickel and nitric oxide react with incandescence at 150°.

Nitric Oxide and Cobalt Tetracarbonyl.

The fact tbat it is comparatively easy to decompose cobalt tetracarbonyl into the tricarbonyl and carbon monoxide shows that one of the carbon monoxide radicles is only slightly attached to the tetracarbonyl molecule. Hence it seemed probable tbat it should be possible to replace the slightly bonded radicle by another group. Such, in fact, proved to be the case.

Slowly at room temperature, but almost instantaneously at 40°, nitric oxide gas reacts with cobalt tetracarbonyl to form a cherry-red liquid, with the evolution of carbon monoxide.

We prepared several cubic centimetres of the liquid as follows :— Pure, dry nitric oxide was slowly passed through a tube of the carbonyl at 40°. The brown crystals of the carbonyl were rapidly converted into a deep red liquid, the vapour of which had a deep red colour. The tube was tben heated at 60°, and the liquid distilled, in a current of nitric oxide, into a cooled receiver. The exit gases were collected, measured, and analysed : 3·1309 grams of $Co(CO)_4$ gave 2·7112 grams of the red liquid, 0·3612 gram of residual $Co(CO)_3$, and 407·6 c.c. of carbon monoxide (at N.T.P.).

Now the 0·3612 gram of $Co(CO)_3$ resulted by the evolution of 56·4 c.c. of carbon monoxide from 0·4317 gram of $Co(CO)_4$.

Therefore the 2·7112 grams of the red liquid were obtained by

the action of nitric oxide on 2·6992 grams of $Co(CO)_4$, with the evolution of 351·2 c.c. of carbon monoxide, or exactly one-fourth of the carbon monoxide in the carbonyl. The yield of liquid was 100·5 per cent. of the weight of the carbonyl reacting with the nitric oxide. Obviously, therefore, the reaction between nitric oxide and cobalt tetracarbonyl is represented by the following equation:

$$Co(CO)_4 + NO = Co(CO)_3{\cdot}NO + CO.$$

The liquid was analysed (Found: Co = 33·41; CO = 50·09; NO = 17·30 per cent.).

The red liquid is therefore cobalt nitrosotricarbonyl, $Co(CO)_3{\cdot}NO$.

Properties of Cobalt Nitrosotricarbonyl.—This substance is a cherry-red, mobile liquid, very volatile, and remarkably stable under water, in which it is insoluble. It is miscible in all proportions with alcohol, benzene, ether, chloroform, etc. It may be distilled in a current of inert gas at 50—60° with only slight decomposition into cobalt tricarbonyl and nitric oxide. The density at 14° is 1·5126, and the melting point − 1·05°.

Only 0·5 c.c. was available for the determination of the boiling point, and the usual procedure could not be followed. We therefore used the method of O'Dowd and Perkin (*Trans. Faraday Soc.*, 1908, **4**, 95). This gave excellent results, and we found the boiling point of the nitroso-carbonyl to be 78·6° at 761 mm.

The molecular weight, as determined by Victor Meyer's method, is 171·7 [$Co(CO)_3{\cdot}NO$ requires M = 173].

The vapour pressure is as follows:—

Temperature.	Vapour pressure in mm. of mercury.	Temperature.	Vapour pressure in mm. of mercury.
14°	77	45°	251
23	100	56	361
36	171	66	517

Above 66°, the compound slowly decomposes.

Nitric Oxide and Cobalt Tricarbonyl.

Up to 60° nitric oxide did not react with cobalt tricarbonyl. At 75—80° there appeared to be very slight reaction, but the amount of the product was too small to be collected.

Nitric Oxide and Iron Carbonyls.

The reaction of nitric oxide with cobalt tetracarbonyl led us to examine the different iron carbonyls, with the following results.

There is no reaction between nitric oxide and diferrononacarbonyl at temperatures up to 60°. At 63°, slight reaction occurs and beads of red liquid appear. At 100°, the reaction is complex. At first the liquid pentacarbonyl, containing some tetracarbonyl, appears, and after a time the whole decomposes with much violence. At 70—85°, the reaction is regular; the solid iron carbonyl gradually disappears as the red liquid is formed.

In our early experiments we observed that only a small amount of carbon monoxide was evolved, and therefore the reaction taking place could not, as we had expected, be represented hy the equation

$$Fe(CO)_5 \cdot Fe(CO)_4 + 4NO = Fe(CO)_5 \cdot Fe(NO)_4 + 4CO.$$

Further, on repeated distillation of the red liquid, the colour disappeared and pure pentacarbonyl remained, in bulk almost equal to that of the original liquid. In the distilling flask was found a small amount of hrown powder, which appeared to be a compound of iron and nitric oxide.

Several experiments gave the following results :—

Carhon monoxide evolved = 11·4—11·8 per cent.

Yield of the red liquid = 92—95 per cent. [Found : Fe = 30; NO = 4·34; CO = 65·60. $C_3O_{16}NFe_4$ requires Fe = 33·0; NO = 4·4; CO = 62·6 per cent.].

The reaction between nitric oxide and diferrononacarbonyl must therefore be represented by the equation

$$2Fe_2(CO)_9 + NO = FeNO,3Fe(CO)_5 + 3CO.$$

The theoretical yield would be 92·6 per cent., with the evolution of 11·5 per cent. of carhon monoxide.

The composition differs by 3 per cent. in iron and in carhon monoxide from the analysis of the red liquid, but greater accuracy could not be expected, owing to the difficulties of manipulation, with the very small amounts of liquid available for analysis. The properties of this iron nitroso-carbonyl are very similar to those of the cohalt compound. We have not as yet determined its boiling point, freezing point, etc.

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VII.—*Organo-derivatives of Thallium. Part III. Some Thalliumdialkyl Salts and the Preparation of Thalliumdiaryl Haloids.*

By Archibald Edwin Goddard.

In a previous communication (Goddard, T., 1921, **119**, 672) it was shown that thalliumdialkyl haloids reacted readily with silver salts. This has now been utilised in the preparation of thalliumdiethyl nitrite and lactate, the former showing a similar stability to the corresponding nitrate. Since the author was unable to obtain thalliumdi*iso*propyl iodide, it was thought possible that the larger the aliphatic group attached to the thallium the less stable the compound might become. To test this the thalliumdiethyl salts were prepared from the formate up to the *n*-octoate, and the series shows a fall of melting point with rise of molecular weight and an increase of solubility. The formate, however, was not obtained pure for analysis, but the specimen gave a melting point 240—241°. The salts were prepared by the action of thalliumdialkyl hydroxides on the respective acids (see Cahours and Demarçay, *Compt. rend.*, 1879, **88**, 1112). The thalliumdiethyl acetate, m. p. 232—233°, appears to be purer than that obtained by Hartwig (*Ber.*, 1874, **7**, 298), which melted at 212°.

Three salts in the aromatic series, namely, thalliumdiethyl *p*-nitrobenzoate, *p*-iodobenzoate, and *m*-bromobenzoate have also been obtained. Magnesium *iso*butyl and *iso*amyl iodides react with thallic chloride in a similar manner to magnesium *iso*propyl iodide, causing quantitative reduction to thallous iodide.

Concentrated hydrochloric acid, thionyl chloride, ammonia gas, and mercuric chloride do not react with thalliumdiethyl chloride, but iodine trichloride even in the cold violently attacks the corresponding bromide, with the production of thallous iodide. This appears to be due to the action of chlorine in the presence of iodine, since solid iodine added to a boiling aqueous solution of thalliumdiethyl hromide has practically no action.

Meyer and Bertheim (*Ber.*, 1904, **37**, 2051), by the action of magnesium phenyl bromide on thallic chloride, obtained a compound stated to be thalliumdiphenyl bromide, which could not be prepared pure for analysis. It was also stated that on heating with fuming nitric acid for several hours in a sealed tube at 300°, the substance was not completely decomposed. The author has now obtained thalliumdiphenyl chloride, which does not melt at 288°. in a pure

state, and finds that it is decomposed by fuming nitric acid even in the cold, and claims therefore that this is the first organo-derivative of thallium in the aromatic series to be produced. The product was obtained by the interaction of triphenylbismuthine and thallic chloride in cold anhydrous ether. Considerable difficulty was experienced in purifying the compound, this probably being due to a secondary reaction which produced small quantities of thalliumphenyl dichloride and inorganic derivatives of thallium, the reaction being represented as taking place in two stages :

1. $2(C_6H_5)_3Bi + TlCl_3 = 2(C_6H_5)_2BiCl + (C_6H_5)_2TlCl.$
2. $(C_6H_5)_2TlCl + TlCl_3 = 2C_6H_5 \cdot TlCl_2.$

The reaction represented by the second equation is at present under investigation.

The compound thus formed is identical in properties with that produced from mercury diphenyl and thallic chloride in ethereal solution. Triphenylstibine and thallic chloride, however, react quantitatively and immediately in the cold in accordance with the equation :

$$(C_6H_5)_3Sb + TlCl_3 = (C_6H_5)_3SbCl_2 + TlCl.$$

In the case of triphenylarsine, a precipitate of yellow scales will be obtained after some time; the reaction is still under investigation.

EXPERIMENTAL.

Thalliumdiethyl Nitrite.—Two grams of thalliumdiethyl iodide and 0·9 gram of silver nitrite were shaken in 70 c.c. of acetone, and the mixture was kept over-night. The precipitated silver iodide was filtered off and extracted with acetone, these washings being added to the main filtrate; this, on evaporation, yielded 1·0 gram of large, transparent plates, which did not melt at 290° (Found : N = 4·54; Tl = 66·14. $C_4H_{10}O_2NTl$ requires N = 4·54; Tl = 66·17 per cent.). The nitrite is completely soluble in hot pyridine and insoluble in other organic solvents.

Thalliumdiethyl Lactate.—This was prepared in the way described above, 1·5 grams of silver lactate being employed. The product (1·5 grams), after four crystallisations from alcohol, gave small plates which suddenly decomposed without melting at 267·5° (Found : Tl = 58·13. $C_7H_{15}O_3Tl$ requires Tl = 58·04 per cent.). The lactate is soluble in cold water, acetone, or alcohol, and easily soluble in boiling chloroform, toluene, or ethyl acetate.

Thalliumdimethyl Acetate.—By acidifying the hydroxide derived from 2·0 grams of thalliumdimethyl iodide with acetic acid and concentrating the solution, 1·2 grams of long, elongated plates were deposited, m. p. 293° (Found : Tl = 70·17. $C_4H_9O_2Tl$ requires

Tl = 69·56 per cent.). The salt is very soluble in water, alcohol, or acetone, less soluble in ether or petroleum.

Thalliumdiethyl Acetate.—By the interaction of the hydroxide from 3·42 grams of thalliumdiethyl bromide and 0·70 gram of acetic acid, 0·8 gram of short, white needles was obtained. After two crystallisations from water, these melted at 232—233° (Found: Tl = 63·25. $C_6H_{13}O_2Tl$ requires Tl = 63·47 per cent.). The solubility of this salt is the same as the above.

Thalliumdiethyl Propionate.—Using in this case 0·5 gram of propionic acid, 0·9 gram of fine, short needles was obtained on concentration, m. p. 228—229° (Found: C = 24·70; H = 4·65; Tl = 60·09, 60·54. $C_7H_{15}O_2Tl$ requires C = 25·14; H = 4·51; Tl = 60·66 per cent.). The salt is completely soluble in hot alcohol, ethyl acetate, toluene, or acetone, in cold pyridine or chloroform, moderately soluble in hot ether or carbon tetrachloride, and slightly soluble in light petroleum.

Thalliumdiethyl Valerate.—By the interaction of the hydroxide from 3·42 grams of thalliumdiethyl bromide and 1·07 grams of valeric acid, 1·9 grams of small needles were obtained, m. p. 215° (Found: C = 29·20; H = 5·21; Tl = 56·00, 56·04. $C_9H_{19}O_2Tl$ requires C = 29·85; H = 5·27; Tl = 56·11 per cent.). The salt is completely soluble in cold alcohol, ether, pyridine, chloroform or hot carbon tetrachloride, moderately soluble in cold toluene, acetone, or ethyl acetate, and insoluble in light petroleum.

Thalliumdiethyl Hexoate.—Prepared, in the way described above, from 2 grams of the bromide and 0·73 gram of the acid, 1·2 grams of product were obtained, which on crystallisation from acetone and light petroleum gave transparent needles half an inch in length, softening at 182° and melting at 190° (Found: Tl = 54·04. $C_{10}H_{21}O_2Tl$ requires Tl = 54·02 per cent.). With the exception of its solubility in light petroleum, it agrees in all respects with the valerate.

Thalliumdiethyl n-*Octoate.*—By means of 0·89 gram of *n*-hexoic acid, a hard solid mass (1·3 grams) insoluble in water was obtained. This was crystallised twice from light petroleum, when long, transparent needles, m. p. 159°, were deposited (Found: Tl = 50·23, 50·03. $C_{12}H_{25}O_2Tl$ requires Tl = 50·27 per cent.). The salt resembles the hexoate in its solubility.

Thalliumdiethyl p-*Nitrobenzoate.*—To the hydroxide from 2 grams of thalliumdiethyl bromide was added 0·98 gram of *p*-nitrobenzoic acid, and the mixture was boiled and concentrated. The resulting solid, 1·2 grams, was crystallised twice from chloroform, when microscopic needles were obtained, m. p. 213° (Found: N = 3·59; Tl = 47·19. $C_{11}H_{14}O_4NTl$ requires N = 3·27; Tl = 47·59 per cent.). The salt is completely soluble in cold pyridine, moderately

soluble in alcohol or chloroform, slightly soluble in carbon tetrachloride, toluene, ethyl acetate, or acetone, and insoluble in ether or light petroleum.

Thalliumdiethyl p-*Iodobenzoate.*—1·45 Grams of *p*-iodobenzoic acid being employed, 2·0 grams of small, white needles containing iodine were deposited. These decomposed with slight explosion at 220° (Found: Tl = 39·70. $C_{11}H_{14}O_2ITl$ requires Tl = 40·03 per cent.). The solubility is similar to that of the above nitro-compound.

Thalliumdiethyl m-*Bromobenzoate.*—This was prepared in the usual manner, from 1·18 grams of *m*-bromobenzoic acid. The small, white needles (1·6 grams) obtained after two crystallisations from water melted with considerable gas evolution at 220° (Found: Tl = 43·49. $C_{11}H_{14}O_2BrTl$ requires Tl = 44·10 per cent.). The above compound is insoluble in acetone, but otherwise resembles the nitrobenzoate.

Action of Iodine Trichloride on Thalliumdiethyl Bromide.

To a suspension of 1·45 grams of the bromide in 40 c.c. of light petroleum 1·7 grams of iodine trichloride were slowly added, and an immediate liberation of iodine was noticed. After remaining over-night, the whole was boiled and filtered. All free iodine having been washed from the residue, the latter was found to be thallous iodide (Found: I = 61·91. Calc., I = 61·64 per cent.). The same result was obtained when the reaction was carried out in the cold.

Action of Magnesium iso*Amyl Iodide and of Magnesium* iso*Butyl Iodide on Thallic Chloride.*

A solution prepared from 28·0 grams of *iso*amyl iodide and 3·2 grams of magnesium in dry ether was slowly added to a solution of 7·13 grams of thallic chloride in the same solvent. After standing half an hour, the solution was decomposed, but no trace of organic matter was found in the residue and 6·95 grams of thallous iodide were isolated. As the original thallic chloride should have yielded 7·61 grams, quantitative reduction had occurred.

The same result was obtained when magnesium *iso*butyl iodide was used.

Action of Triphenylbismuthine on Thallic Chloride.

Sufficient dry ether was added to 5·0 grams of triphenylbismuthine to effect solution, followed by 3·54 grams of thallic chloride in the same solvent. A white precipitate was immediately thrown

down, and after remaining for a short time the whole became solid. The precipitate was filtered off and repeatedly shaken with acetone until the extract gave no solid on evaporation. The residue thus obtained (3·75 grams) was organic and contained thallium, but was not pure for analysis. Purification was carried out by crystallising from pyridine, then boiling with glacial acetic acid, and further crystallising from pyridine, the product being thoroughly washed with boiling acetone (Found: Tl = 51·44, 51·51, 51·71; Cl = 9·26, 9·01. $C_{12}H_{10}ClTl$ requires Tl = 51·84; Cl = 9·01 per cent.). *Thalliumdiphenyl chloride* crystallises from pyridine in colourless, microscopic needles which do not melt at 288° and are slightly soluble in boiling acetic acid, alcohol, ethyl acetate, or chloroform, and insoluble in ether, acetone, or light petroleum.

The above acetone extracts on evaporation gave 4·0 grams of diphenylchlorobismuthine (m. p. 185—186°), but no unchanged bismuthine, and traces of inorganic thallium products.

Preparation of Thalliumdiphenyl Chloride by means of Mercury Diphenyl.

To a solution of 2·8 grams of mercury diphenyl in 50 c.c. of dry ether, 2·5 grams of thallic chloride in the same solvent were added, when a white precipitate was immediately thrown down. After remaining for several hours, this was filtered off and extracted with benzene in a Soxhlet apparatus. The benzene removed some mercury phenyl chloride, m. p. 250°, and the residue, after purification, was analysed (Found: Tl = 51·51; Cl = 9·09. Calc., Tl = 51·84; Cl = 9·01 per cent.).

Action of Triphenylstibine on Thallic Chloride.

To a solution of 5·25 grams of the stibine in 50 c.c. of toluene, 3·1 grams of thallic chloride in 4·8 c.c. of ether were added. An almost white precipitate was immediately thrown down, which was filtered off after twenty-four hours. The residue (3·2 grams) was found to be thallous chloride. The filtrate, on evaporation, yielded 3·6 grams of triphenylstibine dichloride (m. p. 143°), no unchanged stibine being obtained. The process is therefore merely one of chlorination by thallic chloride.

The author is indebted to the Research Fund of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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VIII.—*The Rate of Solution of Iron in Dilute Sulphuric Acid both when Stationary and under Rotation.*

By JOHN ALBERT NEWTON FRIEND and JOHN HORACE DENNETT.

IT having recently been observed that iron does not rust when exposed to the action of water and air in rapid motion (Friend, T., 1921, **119**, 932), it appeared of interest to determine whether or not the rate of solution of iron in acids is likewise retarded by movement. A study has therefore been made of the action of dilute sulphuric acid on Kahlbaum's pure electrolytic iron foil under varying conditions. The work is not yet completed, having been temporarily suspended in consequence of the departure of one of the authors; but it was thought desirable to place on record the results so far obtained, in view of their important bearing on recent researches on corrosion.

Influence of Temperature.

Almost nothing is known as to the quantitative effect of rise of temperature on the rate of solution of iron in acid. Small pieces of foil, 5 × 2·6 sq. cm. in area, were suspended from glass hooks in large jars containing 600 c.c. of *N*-sulphuric acid and kept at various temperatures for seventy-five minutes. The plates were then removed, washed, dried, and weighed. The results were as follows :

Temp.	Loss in weight. Gram.	Mean loss.	Relative rate of solution.
0°	0·003 (calc).	—	1·00
2·3	0·0050 0·0060	0·0055	1·83
13·0	0·0170 0·0224	0·0197	6·57
28·7	0·0356 0·0337	0·0346	11·5
45·0	0·0830 0·0742	0·0786	26·2
58·5	0·2296 0·1490	0·1893	63·1

The rate of solution is taken as unity at 0°, the value being calculated by extrapolation from the curve. The values of the relative rates of solution, when plotted against the temperature, are seen to lie on a hyperbolic curve analogous to that recently found by Seligman and Williams (*J. Soc. Chem. Ind.*, 1916, **35**, 665) representing the rate of solution of aluminium in nitric acid with rise of temperature.

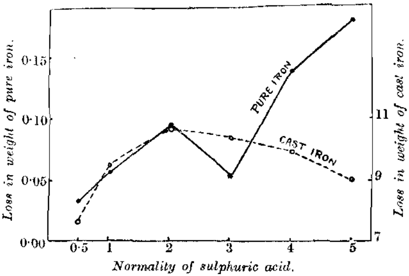
Influence of Acid Concentration.

This was determined at about 15° by allowing similarly sized plates of foil to the preceding to hang from glass hooks, each in four litres of sulphuric acid. The losses in weight after thirty-four hours were regarded as a measure of the rate of solution. The results were as follows:

Normality of acid	0·5	1	2	3	4	5
Loss in weight of iron...	0·0338	0·0547	0·0961	**0·0511**	0·1380	0·1531

The results are shown in Fig. 1. A remarkable feature is the breaks in the curve with $2N$- and $3N$-acid. The experiments have been repeated several times, but always with the same result. In

FIG. 1.



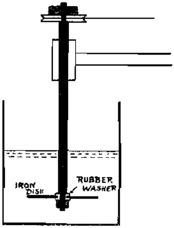
the case of cast iron, a maximum rate of solution has been found near this concentration, the exact point varying a little with the composition of the metal. Some results obtained by Messrs. Catch and Hargest, working in the authors' laboratory, are indicated by the broken line in the figure. The cast iron contained graphite, 2·75; combined C, 0·55; Si, 2·28; Mn, 0·69; S, 0·076; P, 1·04 per cent. The coincidence between these maxima is interesting, and no satisfactory explanation for either is apparent.

Influence of Motion.

The apparatus finally adopted is shown in Fig. 2, and consisted of a 1/4 H.P. electric motor capable of giving 1700 revs. per min. Its pulley was connected by a small leather driving-belt with one screwed on to a gun-metal axle, the lower end of which carried the

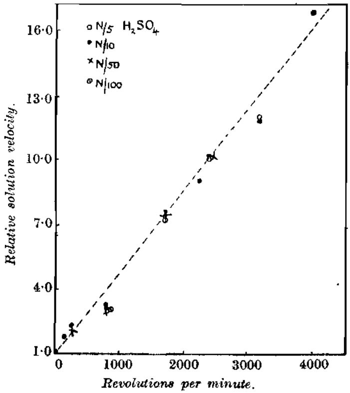
iron foil in the form of a disk 7·5 cm. in diameter. This disk was fixed with a nut on to the axle, contact with both nut and axle being prevented by the use of rubber washers. The axle was supported vertically by a rigid clamp, free rotary motion being obtained with ball bearings as in a cycle hub. By using various sizes of pulleys, speeds ranging from 145 to 4000 revs. per minute were obtainable. These were read off at intervals during the experiments from a speedometer.

FIG. 2.



The lower end of the axle carrying the iron disk was lowered into a glass tank, the internal walls of which possessed raised vertical ribs—a device that greatly reduced the tendency of the liquid to swirl round with the rotating disk. The experiments lasted for thirty minutes each, and the volume of liquid was the same in every

FIG. 3.



case, namely, 1 litre. The amount of iron dissolved was estimated by titration with permanganate. Before each experiment the iron disk was carefully polished with emery, the same disk being used

throughout in order to avoid fluctuations due to chemical and physical differences in the metal, so characteristic of different specimens of even the purest forms of iron. The results are shown graphically in Fig. 3.

It will be observed that:

1. The different concentrations of acid yield almost identical results at the same velocities.

2. The rate of solution is directly proportional—within the error of experiment—to the velocity of rotation. Even at 4000 revolutions, corresponding with a rim velocity of 35 miles per hour, there is no sign of falling off in the rate of solution. Evidently, therefore, solution of iron in acid is a different process from the corrosion of iron in aerated water. In the latter case, corrosion ceases at a velocity of 3 to 5 miles per hour.

Influence of Colloids.

A few experiments have been carried out on the rate of solution of stationary iron in sulphuric acid in the presence of protective colloids such as gum acacia. It is found that dilute solutions of this gum greatly retard the solution of the metal, just as they have been shown (Friend, *loc. cit.*) to retard the corrosion of iron in neutral solution. Mr. Trobridge, working in the authors' laboratory, has shown that a similar retardation occurs with hydrochloric acid, so that this action of the colloids appears to be general.

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IX.—*The Action of Sulphuryl Chloride on Organic Substances. Part I. Simple Monosubstituted Benzenes.*

By THOMAS HAROLD DURRANS.

SULPHURYL chloride reacts readily with a large number of organic substances, generally functioning either as a chlorinating or as a dehydrating agent. Its action as a chlorinating agent is frequently, but not always, similar to that of chlorine, and sometimes to that of phosphorus pentachloride, whilst in its dehydrating action it resembles sulphur trioxide. Thus, in the absence of a catalyst, it

chlorinates benzene, toluene, phenol, anisole, phenetole, or aniline, and with salts of acids, such as sodium benzoate or acetate, it yields the corresponding acid anhydride and acid chloride (compare Dubois, *Bull. Acad. roy. Belg.*, 1876, **42**, 126; Wöhl, D.R.-P. 139552; Wenghöffer, *Ber.*, 1877, **10**, 441; Peratoner, *Gazzetta*, 1894, **24**, i, 236).

Although a large amount of work has already been done in this connexion, there is a lamentable lack of information regarding the action of sulphuryl chloride on the organic substances in common use. This investigation is designed to contribute a small addition to our existing knowledge in this direction.

The conditions of experiment have been those obtaining when the organic suhstance is boiled under atmospheric pressure for several hours with a large excess of sulphuryl chloride; consequently the products isolated represent the final products to be obtained in such circumstances, the isolation of any intermediate product not having been aimed at. The table shows briefly the results obtained:

Organic Substance.	Product.
Benzaldehyde	Benzoyl chloride.
Phenylacetonitrile	Phenyldichloroacetonitrile.
Acetophenone	ωω-Dichloroacetophenone.
Benzophenone	No action.
Nitrobenzene	,, ,,
Sodium benzenesulphonate	,, ,,
Sodium phenoxide (aqueous)	*p*-Chlorophenol.
,, ,, (anhydrous)	2 : 3 : 4 : 6-Tetrachlorophenol.
Triphenyl phosphate	No action.
,, ,, in presence of iron	Tri-*p*-chlorophenyl phosphate.
Sodium phenylacetate	Phenylacetic anhydride and phenylacetyl chloride.
Benzamide	Traces of benzonitrile only.

Phenylethyl alcohol yields an unstable product, probably a mixture of phenylethyl sulphate and phenylethyl chloride, the reaction being similar to that with benzyl alcohol (Bebrend, *J. pr. Chem.*, 1877, [ii], **15**, 23).

EXPERIMENTAL.

Benzaldehyde.—Sulphuryl chloride (5 mols.) was distilled on to benzaldehyde (1 mol.); no sensible reaction took place. The mixture was slowly distilled until the excess of sulphuryl chloride was removed, the residue being distilled under reduced pressure. After repeated distillation, a fraction, b. p. 195—200°/760 mm., was obtained (benzoyl chloride boils at 198°), the only other substance present in any appreciable quantity being benzaldehyde; a small amount of tarry matter was formed (Found: Cl = 24·69. Calc., Cl = 25·27 per cent.).

The substance was identified with benzoyl chloride by conversion into benzoic acid and ethyl benzoate. The action of sulphuryl chloride on benzaldehyde is therefore similar to that of chlorine, but differs in that the simultaneous formation of traces of benzyl chloride does not appear to take place.

Phenylacetonitrile.—This substance (1 mol.) was treated with sulphuryl chloride (5 mols.) as in the foregoing experiment; the residual liquid distilled at 115°/20 mm.

The fraction was highly lachrymatory, but otherwise almost devoid of odour. It would not solidify when cooled to −15° (Found: Cl = 38·52. $C_6H_5{\cdot}CCl_2{\cdot}CN$ requires Cl = 38·18 per cent.).

The substance, when boiled with alcoholic sodium hydroxide solution, immediately deposited sodium chloride and evolved first a slight odour of hydrocyanic acid and then one of ammonia. On pouring the mixture into water and acidifying, benzoic acid was deposited; this, twice crystallised from water, melted at 120·5°. The acid was further identified by means of a mixed-melting point determination and of its ethyl ester, b. p. 213°.

The substance, heated on a steam-bath with an equal weight of 75 per cent. sulphuric acid for three hours, yielded, on cooling, a precipitate of benzoic acid. It is clearly phenyldichloroacetonitrile and is identical with the substance obtained by Claisen (*Ber.*, 1879, **12**, 626).

Acetophenone.—Sulphuryl chloride (3 mols.) was slowly distilled on to acetophenone (1 mol.), and a vigorous reaction ensued. When this had subsided, the excess of sulphuryl chloride was slowly distilled off; the residual liquid distilled at 124—140°/12 mm. By repeated fractional distillation a fraction boiling at 121—122°/10 mm. and at 245°/760 mm. was obtained, which could not be made to solidify even at −10° (Found: C = 50·12; H = 3·16; Cl = 38·45. $C_8H_6OCl_2$ requires C = 50·79; H = 3·17; Cl = 37·58 per cent.).

When the substance was boiled for several hours with *N*/10-aqueous-alcoholic silver nitrate, only a trace of silver chloride was formed, this probably arising from an impurity in the substance. The substance was not oxidised by chromic acid mixture, but yielded readily to alkaline permanganate solution, a faint odour of chloroform being evolved. This chloroform probably arose from a trace of the trichloride, $C_6H_5{\cdot}CO{\cdot}CCl_3$, the presence of which would account for the slightly high chlorine content. From the mixture obtained by the alkaline permanganate oxidation, benzoic acid was isolated in good yield.

The chief substance resulting from the reaction between acetophenone and sulphuryl chloride is therefore ωω-dichloroaceto-

phenone and is identical with the ketone obtained by Gautier (*Ann. Chim. Phys.*, 1888, [vi], **14**, 348).

Sodium Phenoxide.—The action of sulphuryl chloride on the sodium salts of certain acids is to produce the acid anhydride and the acid chloride. It was thought possible that with sodium phenoxide diphenyl ether or phenyl sulphate might result. There was also the possibility that in aqueous solution a reaction similar to the Schotten-Baumann reaction might take place, whilst a fourth possibility was that its action would be similar to that with phenol, where *p*-chlorophenol is obtained. Two experiments were therefore conducted.

A large excess of sulphuryl chloride was slowly distilled on to carefully dried sodium phenoxide, a very vigorous reaction taking place. The excess of sulphuryl chloride was distilled off and the solid remaining extracted with benzene. After the removal of the benzene from the extract, a liquid remained which had an initial boiling point of about 150°/17 mm. A fraction, b. p. 190—210°/17 mm., was collected, and this solidified on cooling. The residue was black and evolved hydrogen chloride.

The solid was insoluble in sodium carbonate solution but readily soluble in sodium hydroxide solution, from which it was precipitated on acidifying. It did not contain sulphur and was therefore not phenyl sulphate. Crystallised three times from ether, it melted at 65—66°. Its benzoyl derivative had m. p. 116° (compare Zincke and Wallhaum, *Annalen*, 1891, **261**, 246) (Found: C = 31·2; H = 1·22; Cl = 61·4. $C_6H_2OCl_4$ requires C = 31·0; H = 0·86; Cl = 61·2 per cent.).

The fractions of lower boiling point obtained in small yield were redistilled and a small fraction, b. p. about 217°/760 mm., was obtained (*p*-chlorophenol boils at 217°). This, on cooling and seeding with a crystal of *p*-chlorophenol, solidified immediately, and after drying on a porous tile had m. p. 40°. The substance was identified with *p*-chlorophenol.

The substances produced by the action of sulphuryl chloride on anhydrous sodium phenoxide are therefore *p*-chlorophenol and a tetrachlorophenol, probably the 2 : 3 : 4 : 6-isomeride obtained by Zincke and Schaum (*Ber.*, 1894, **27**, 549).

The reaction in aqueous solution was conducted as follows: ninety-four grams of phenol were dissolved in a solution of 40 grams of sodium hydroxide in 200 grams of water, and the excess of phenol was removed by boiling under diminished pressure. Seventy grams of freshly-distilled sulphuryl chloride were then added to the cold solution, with shaking and cooling in iced water. An oil formed and was separated, dried, and distilled, the b. p.

86°/22 mm. rising to 145°/16 mm. The distillate, which solidified on cooling, was dissolved in sodium carbonate solution and a small portion of insoluble oil (phenol) removed by extraction with ether; on acidifying, an oil was obtained which had b. p. 215—217° (*p*-chlorophenol boils at 217°) and m. p. 42°. The substance was identified with *p*-chlorophenol.

Triphenyl Phosphate.—Sulphuryl chloride is almost entirely without action on triphenyl phosphate when boiled with it under atmospheric pressure (compare Peratoner, *Gazzetta*, 1898, **28**, i, 197), but in the presence of quite small quantities of iron tri-*p*-chlorophenyl phosphate is readily formed.

No reaction having been found to take place between triphenyl phosphate and sulphuryl chloride under the usual conditions, an addition of 1 per cent. of 60-mesh iron filings was made and the mixture heated under reflux for ten hours. After the excess of sulphuryl chloride had been distilled off, the residue was poured into water, well washed, and neutralised. The solid, after crystallising three times from alcohol, melted at 113° (Found: C = 49·95; H = 3·00; Cl = 24·46. $C_{18}H_{12}O_4Cl_3P$ requires C = 50·29; H = 2·79; Cl = 25·08 per cent.).

The substance was hydrolysed with 2*N*-alcoholic sodium hydroxide, the product poured into water, acidified, extracted with benzene, and the extract distilled. The main fraction, after removal of the benzene, boiled at 210—220° and when seeded with *p*-chlorophenol solidified (m. p. 40°). Dried on porous tile and reprecipitated from sodium carbonate solution, the substance melted at 43° (Found: Cl = 27·22. Calc., Cl = 27·63 per cent.).

It follows, therefore, that the substance obtained by the action of sulphuryl chloride on triphenyl phosphate in the presence of iron is tri-*p*-chlorophenyl phosphate.

Benzamide.—Sulphuryl chloride (9 mols.) was distilled on to benzamide (1 mol.), no apparent reaction ensuing. The sulphuryl chloride was very slowly distilled off and the residue distilled under reduced pressure. A small early fraction was obtained and the contents of the distillation flask then solidified. The solid, crystallised twice from benzene, had m. p. 124—125° and b. p. 290° and was therefore unchanged benzamide (Found: C = 69·61; H = 5·67. Calc., C = 69·4; H = 5·79 per cent.).

The early fraction from the distillation had b. p. 80°/15 mm. and an odour similar to that of benzaldehyde. It dissolved in hot water and was redeposited on cooling. When it was boiled with sodium hydroxide solution, ammonia was slowly evolved and, on acidifying, benzoic acid was deposited (m. p. 120°). The substance is evidently benzonitrile (Found: N = 13·57. Calc., N = 13·59 per cent.)

formed by the dehydration of the benzamide. Sulphuryl chloride therefore does not attack benzamide except to a small extent to form benzonitrile.

Sodium Phenylacetate.—Freshly-distilled sulphuryl chloride (1·5 mols.) was slowly run on to anhydrous sodium phenylacetate (m. p. about 150°). The excess of sulphuryl chloride was removed in the cold under diminished pressure and the residue distilled as far as possible, a fraction boiling up to 100°/12 mm. being obtained. The solid remaining in the flask was extracted with benzene, and the extract distilled. After the removal of the benzene, a fraction, b. p. 130—168°/12 mm., was obtained which solidified. The solid, twice crystallised from benzene, had m. p. 75°. 1·235 Grams, boiled with *N*-aqueous-alcoholic sodium hydroxide, consumed 9·8 c.c., equivalent to 1·245 grams of phenylacetic anhydride. On acidifying a more concentrated similar solution, phenylacetic acid was deposited which, twice crystallised from water, had m. p. 76°.

The early fraction boiling up to 100°/12 mm. was redistilled, and a small fraction, b. p. 93—96°/12 mm., obtained, which fumed slightly in the air. This substance, on hydrolysis, yielded phenylacetic acid, m. p. 76°, and was evidently phenylacetyl chloride (Found: Cl = 23·06. Calc., Cl = 22·98 per cent.).

The products of the reaction between sulphuryl chloride and anhydrous sodium phenylacetate are phenylacetic anhydride and phenylacetyl chloride.

I have to express my indebtedness to Mr. F. Hall, of this laboratory, for most kind assistance in conducting the combustions necessary for this investigation.

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OXFORD. [*Received, June 16th*, 1921.]

X.—*The Formation of Substituted Succinic Acids from Esters of αβ-Unsaturated Acids.*

By LUCY HIGGINBOTHAM and ARTHUR LAPWORTH.

IT was shown by Bredt and Kallen (*Annalen*, 1896, **293**, 350) that hydrogen cyanide forms compounds with alkylidenemalonic esters, addition taking place at the ethylenic linking, and numerous instances of similar additions to the molecules of αβ-unsaturated ketones and nitriles have since been found. These may all be re-

garded as special instances of a general type of additive process represented as follows :

$$>\underset{+}{C}=\underset{-}{\dot{C}}-\underset{+}{X}-\underset{-}{Y}+\underset{+}{H}\cdot\underset{-}{(CN)} \rightarrow >\underset{CN}{C}-\dot{C}H-X-Y,$$

where the attached signs are used to indicate what have been termed the "polarities" of the atoms or groups concerned (compare Fry, *Z. physikal. Chem.*, 1911, **76**, 385, 398, 591; *J. Amer. Chem. Soc.*, 1908, **30**, 34; 1912, **34**, 664; 1914, **36**, 284, etc. Haneke and Koessler, *J. Amer. Chem. Soc.*, 1918, **40**, 1726. Compare also Vorländer, *Ber.*, 1919, **52**, [*B*], 263; *Annual Reports*, 1920, **16**, 88; *Manchester Memoirs* [*Trans. Manch. Lit. and Phil. Soc.*, 1920, 3]). The atom $\underset{-}{Y}$ is regarded as the "key-atom" (*Manch. Memoirs, loc. cit.*), and is usually bivalent oxygen or tervalent nitrogen. Although hitherto the hydrogen cyanide additive process has been observed only in such cases where — X — Y is represented by the >CO of ketones and carboxylic derivatives and by the — C⋮N group of nitriles, there is good reason to believe that union of X and Y by a double or treble linking is not essential, since the addition of sodium hydrogen sulphite (which otherwise is certainly regulated by the same laws as the addition of hydrogen or potassium cyanide) takes place to the ethylenic linking of cinnamyl alcohol,

$$C_6H_5\cdot CH{:}CH\cdot CH_2\cdot OH.$$

It is probable, however, that a doubly or trebly linked arrangement of X and Y is the most effective.

There are other conditions which also greatly influence the ease of the additive process. Thus, for example, the presence of two "key-atoms" in certain positions often increases reactivity, as in alkylidenecyanoacetic acids,

$$X-\overset{+}{\underset{+}{C}}H=\overset{-}{\underset{-}{C}}<\begin{matrix}\overset{+}{C}\equiv\overset{-}{N}\\ \underset{+\,-}{CO\cdot OH}\end{matrix},$$

which absorb hydrogen cyanide at the ethylenic linking under conditions in which the corresponding nitriles or unsubstituted acids do not react appreciably (P., 1904, **20**, 245). Again, whilst, as the present authors have found, the esters of alkylidenemalonic acids react very rapidly with cold solutions of potassium cyanide, the free acids (or rather their salts, since the free acids cannot exist in presence of potassium cyanide) do so relatively slowly, if at all. This observation is quite in accordance with the view that the hydrogen cyanide additive process is regulated mainly by the speed at which cyanidion attaches itself to the unsaturated molecules, for it is evident that the addition of hydrogen cyanide to the ionised

salt of an unsaturated carboxylic acid would then tend to be depressed by the mutual repulsions between the cyanidions and the unsaturated anions of the salt of the carboxylic acid; and it seems quite probable that the addition takes place almost exclusively to the un-ionised molecules of the salt.

The addition of hydrogen cyanide to the simple αβ-unsaturated acids, their salts, esters, or amides, has not hitherto been observed. The considerations to which attention has been directed in the preceding paragraph rendered it probable that the addition was likely to be effected most readily by using the esters or amides of the acids rather than the free acids or their salts. The authors have confirmed this, and incidentally found that surprisingly high yields of mono-substituted succinic acids are obtained by boiling the esters of unsaturated acids of the type Alk·CH:CH·CO_2H with aqueous alcoholic solutions of potassium cyanide. In the initial stage of the process, no doubt, the additive product is formed in accordance with the equation

$$\text{Alk·CH:CH·CO}_2\text{Et} + \text{KCN} + \text{H}_2\text{O} = \text{Alk·CH(CN)·CH}_2\text{·CO}_2\text{Et} + \text{KOH},$$

but partial hydrolysis of the product ensues, owing to the potassium hydroxide formed, and ammonia is rapidly evolved. No special attempts have been made to isolate the intermediate products, but the crude products were at once further hydrolysed. In this way, crotonic acid yielded methylsuccinic acid, and Δ^{α}-nonenoic acid gave hexylsuccinamic acid, both in excellent yield. The yields of substituted succinic acid are not nearly so good when there are two alkyl groups instead of one on the β-position, or if the alkyl group is replaced by an aryl group, but small quantities of phenylsuccinic acid and of *as*-dimethylsuccinic acid were obtained from the *ethyl esters of cinnamic acid and ββ-dimethylacrylic acid respectively.*

EXPERIMENTAL.

Methylsuccinic Acid from (a) *Ethyl Crotonate and* (b) *Sodium Crotonate.*

(*a*) Ethyl crotonate (5 grams) was dissolved in alcohol (20 c.c.) and heated on the steam-bath with potassium cyanide (3 grams; 1 mol.) dissolved in water (6 c.c.). Some ammonia was evolved and the solution became yellow. After four hours, excess of barium hydroxide solution was added and the boiling continued until ammonia ceased to be evolved. The whole was evaporated to dryness, and then heated with concentrated nitric acid in order to decompose any crotonic acid. After removing excess of nitric acid

and working up the residue by extraction with ether, 5 grams of crystalline solid were obtained, which, after shaking with chloroform and recrystallisation, formed colourless prisms melting at 110° and had all the properties of methylsuccinic acid.

The equivalent, determined by titration with standard alkali, was 65·3, whilst a dibasic acid, $C_5H_8O_4$, requires 66.

The identification of the acid was completed by preparing from it the anilic acid and the anil, which melted at 150° and 101·5—103° respectively.

Substitution of boiling amyl alcohol for ethyl alcohol in the above synthesis in the hope of increasing the speed of reaction by use of a higher temperature led to very unsatisfactory results. With methyl alcohol as solvent, the yield of methylsuccinic acid from 5 grams of ethyl crotonate was only 3 grams.

(*b*) Five grams of crotonic acid, just neutralised with 40 per cent. aqueous sodium hydroxide, were boiled with 3·3 grams of potassium cyanide in 10 c.c. of water, during which time much ammonia was evolved. After ten hours, excess of sodium hydroxide was added and the heating continued in order to hydrolyse any nitrile or amide present. On working up the product and destroying unchanged crotonic acid by means of nitric acid, 0·7 gram of methylsuccinic acid was obtained.

n-*Hexylsuccinic Acid from Ethyl* Δ^{α}-*Nonenoate.*

Nonenoic acid was prepared from heptaldehyde by Harding and Weizmann's method (T., 1910, **97**, 299) and converted into its ethyl ester. The ester (4·6 grams) was dissolved in ethyl alcohol (20 c.c.) and heated to boiling for five and a half hours after addition of potassium cyanide (2 grams) dissolved in water (8 c.c.). Ammonia was slowly evolved during the whole period. Excess of 30 per cent. aqueous sodium hydroxide was then added, and the boiling continued for about an hour, when evolution of ammonia ceased. The alkaline solution, after cooling, was acidified with dilute sulphuric acid and the resulting white precipitate (4 grams) of *hexylsuccinamic acid*, $C_6H_{13}\cdot CH(CO\cdot NH_2)\cdot CH_2\cdot CO_2H$, filtered off. This product crystallised from dilute alcohol in long needles melting at 125—126° and its equivalent was found to be 200, the number theoretically required for a monobasic acid, $C_{10}H_{19}O_3N$, being 201.

n-Hexylsuccinic acid was prepared from the amic acid by boiling for about twenty minutes with 40 per cent. sulphuric acid, the solid acid which separated on cooling being recrystallised from dilute nitric acid. It melted at 83—84°, and its identification was completed by converting into its anhydride and its anilic acid, which

melted at about 53° and at 120—121° respectively (compare Thorpe and Higson, T., 1906, 89, 1470, who give the melting points of these two derivatives as 57° and 122° respectively).

The foregoing method is probably the most satisfactory one for preparing *n*-hexylsuccinic acid, which is otherwise rather troublesome to obtain in pure condition.

as-*Dimethylsuccinic Acid from Ethyl* ββ-*Dimethylacrylate.*

Potassium cyanide (2·5 grams) dissolved in water (8 c.c.) was added to a solution of ethyl ββ-dimethylacrylate (5 grams) in alcohol (20 c.c.), and the whole heated for six hours on the steam-bath. Excess of aqueous barium hydroxide solution was then added, and the whole boiled for several hours, then acidified with excess of concentrated hydrochloric acid, and evaporated to dryness, during which process the odour of dimethylacrylic acid was very evident. The residue, on extraction with ether, yielded only 0·5 gram of *as*-dimethylsuccinic acid melting at 136—137°; it was identified by means of its sparingly soluble calcium salt and by the properties of its anilic acid, which corresponded precisely with those ascribed to it by Auwers (*Annalen*, 1896, **292**, 189).

On repeating the above synthesis but prolonging the action of the potassium cyanide to three and a half days and hydrolysing the product for four hours with excess of 30 per cent. aqueous sodium hydroxide solution, the yield of crude, solid dimethylsuccinic acid obtained was 1·4 grams—approximating to 30 per cent. of the quantity theoretically possible. ββ-Dimethylacrylic ester thus appears to react with potassium cyanide much more slowly than does ethyl crotonate or nonenoate.

Phenylsuccinic Acid from Ethyl Cinnamate.

Ethyl cinnamate reacts almost as slowly with potassium cyanide as does ethyl ββ-dimethylacrylate. After heating 5 grams of the ester with 1·8 grams of potassium cyanide in 5 c.c. of water and 20 c.c. of alcohol, hydrolysing the product with baryta, and working up the resulting acids by acidification, extraction with ether, and distillation with steam to remove unchanged cinnamic acid, rather less than 1 gram of phenylsuccinic acid (m. p. 166°. Equivalent = 96·2; calc., equiv. = 97) was obtained.

Summary.

Methylsuccinic acid and *n*-hexylsuccinic acid are readily obtained in excellent yield by heating the ethyl esters of crotonic acid and

Δ^{α}-nonenoic acid respectively with aqueous-alcoholic potassium cyanide and hydrolysing the crude products. The esters of ββ-dimethylacrylic acid and cinnamic acid react slowly with this reagent, and give relatively poor yields of *as*-dimethylsuccinic acid and phenylsuccinic acid respectively.

Sodium crotonate reacts slowly with aqueous potassium cyanide solution and some methylsuccinic acid may be obtained from the product.

The work is being continued.

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XI.—*Metallic Derivatives of Nitrophenolic Compounds. Part III. Nitrophenoxides of the Alkali Metals.*

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ALTHOUGH the alkali nitrophenoxides have been previously studied by several investigators, no one had recorded any details of the solubility of the hydrated forms obtained. It would appear from our observations that the higher hydrates crystallise first from aqueous solution, and after the lower ones have separated, compounds appear which are complex, consisting of the normal salt, nitrophenol, and water; for example, the lithium *p*-nitrophenoxide, $2C_6H_4O_3NLi,C_6H_5O_3N,4H_2O$. By heating this compound at 160°, both the free nitrophenol and the water can be driven off. The solubility of this series of salts decreases from lithium to potassium and then increases again as we pass to cæsium. Rubidium and cæsium salts are much more soluble than those of lithium. It has been noted (Morgan and Smith, T., 1921, **119**, 1068) that in the case of the alkali selenodithionates, the potassium salt is again the least soluble of the series.

Korczyński (*Ber.*, 1909, **42**, 167) described a lithium *o*-nitrophenoxide (+ $\frac{1}{2}H_2O$) which we have been unable to obtain, and mentioned the deep red, anhydrous salt. The latter has now been analysed, but it was obtained as a brick-red powder by heating the new orange-yellow complex salt, $C_6H_4O_3NLi,C_6H_5O_3N,H_2O$, at 160°.

Investigation in the *meta*-series has yielded the anhydrous lithium salt and in the *para*-series the above-mentioned complex and anhydrous salts.

Fritzsche (*Annalen*, 1859, **110**, 150) obtained the anhydrous sodium *o*-nitrophenoxide by the action of sodium hydroxide on *o*-nitrophenol in 90 per cent. alcohol; this substance has now been obtained by means of absolute alcohol or of sodium hydrogen carbonate in aqueous solution.

Hantzsch (*Ber.*, 1907, **40**, 330) describes the colour changes undergone by sodium and potassium *m*-nitrophenoxides with elevation of temperature, but mentions no definite compounds. The hydrated sodium salt ($+ 2H_2O$) and the corresponding anhydrous derivative are now described. Fritzsche (*loc. cit.*) described the hydrated sodium *p*-nitrophenoxides ($+ 2H_2O$) and ($+ 4H_2O$) prepared with the aid of sodium hydroxide, but by employing the carbonate in aqueous solution we have obtained the hydrate ($+ 2H_2O$), and by heating this at 160°, the anhydrous salt; the latter, on keeping in an ordinary desiccator, yields the orange hydrate ($+ \frac{1}{2}H_2O$), which slowly reverts in air to the original hydrate ($+ 2H_2O$). It is here to be noted that the anhydrous *para*-salt is deep red and not yellow, as is usual for *para*-compounds, but the latter form has also been obtained by heating the red modification at 200° for three hours and then keeping it in a vacuum desiccator for a similar period.

Post and Mehrtens (*Ber.*, 1875, **8**, 1553) mentioned the hydrated potassium *o*-nitrophenoxide ($+ 1H_2O$), but did not analyse the compound, whilst Fritzsche, employing potassium hydroxide, isolated the hydrate ($+ \frac{1}{2}H_2O$) from absolute-alcoholic solution. By the use of potassium carbonate and *o*-nitrophenol the hydrate ($+ 1H_2O$) has been isolated both in aqueous solution and in absolute alcohol, the latter medium yielding the paler product. Two differently coloured anhydrous salts have been obtained at 180°, the one from the hydrate prepared in water giving a deep red compound, which is stable for a short time and has been analysed. The hydrate isolated from absolute-alcoholic solution gives the red anhydrous compound, but this rapidly turns orange-yellow and can be analysed only in this form. In the *meta*-series the hydrate ($+ 2H_2O$) has been again obtained, and to this is now added the anhydrous salt and the complex derivative, $2C_6H_4O_3NK,C_6H_5O_3N,2H_2O$.

In the *para*-series the hydrate ($+ 1H_2O$) has again been isolated and more completely analysed, but the authors have failed to obtain the hydrates ($+ \frac{1}{2}H_2O$) and ($+ 2H_2O$) described by Fritzsche, and the anhydrous salt is now added to these.

Korczyński (*loc. cit.*) obtained rubidium *o*-nitrophenoxide (+ $\frac{1}{2}H_2O$) by carrying out the reaction in 90 per cent. alcohol, but the authors have isolated the hydrate (+ $1H_2O$) from an aqueous solution. This salt, rubidium *m*-nitrophenoxide (+ $2H_2O$), and the *para*-compound (+ $1H_2O$) are all orange-yellow and almost indistinguishable. It is only when they are dehydrated that they show normal colours. The cæsium salts, on the other hand, show the usual colours even in their hydrated forms. The following were isolated: cæsium *o*-nitrophenoxide (+ $1H_2O$), the *meta*-salt (+ $1H_2O$), the *para*-salt (+ $1H_2O$), and their anhydrous forms.

The solubility of all the above salts is much greater than that of the alkaline-earth nitrophenoxides (Goddard, T., 1921, **119**, 1161), and this accounts for the difficulty of forming hydrates of these compounds.

EXPERIMENTAL.

Derivatives of o-*Nitrophenol*.—$C_6H_4O_3NLi,C_6H_5O_3N,H_2O$, orange-yellow, granular powder [Found: N = 9·35 (9·28) *; Li = 2·83 (2·30); $C_6H_5O_3N + H_2O$ = 52·76 (52·03) per cent.]. $C_6H_4O_3NLi$, brick red [Found: N = 9·46 (9·89); Li = 5·06 (4·90) per cent.]. $C_6H_4O_3NNa$, brilliant red needles [Found: N = 8·48 (8·70); Na = 14·29 (14·28) per cent.]. $C_6H_4O_3NK,H_2O$, prepared in aqueous solution, brilliant orange needles [Found: N = 7·05 (7·18); K = 20·83 (20·03); H_2O = 9·49 (9·23) per cent.]. The same compound, prepared in alcoholic solution, pale orange needles [Found: N = 7·02 (7·18); H_2O = 10·26 (9·23) per cent.]. $C_6H_4O_3NK$, prepared from the hydrated compound obtained from aqueous solution, scarlet, becoming orange in alcohol or toluene and slowly changing to the more stable orange form in the air [Found: N = 7·51 (7·91); K = 22·02 (22·07) per cent.]. The anhydrous salt obtained from the alcoholic preparation, orange yellow, becoming red in pyridine [Found: N = 7·76 (7·91); K = 22·47 (22·07) per cent.]. $C_6H_4O_3NRb,H_2O$, orange-yellow needles, becoming deeper orange in alcohol, acetone, pyridine, carbon tetrachloride or toluene, and melting in hot ethyl acetate [Found: H_2O = 7·54 (7·46) per cent.]. $C_6H_4O_3NRb$, scarlet at 100° and deep yellow at 160°, not reverting to red on cooling. $C_6H_4O_3NCs,H_2O$, fine scarlet needles, becoming orange in acetone, deep red in toluene or ethyl acetate, and melting in the latter [Found: N = 4·51 (4·85); Cs = 46·86 (45·98); H_2O = 6·34 (6·23) per cent.]. $C_6H_4O_3NCs$, deep red [Found: N = 4·86 (5·17); Cs = 50·00 (49·03) per cent.].

* The figures in brackets denote the theoretical percentages.

Derivatives of m-*Nitrophenol.*—$C_6H_4O_3NLi$, shining, ruby-red, short needles [Found: N = 9·69 (9·89); Li = 4·17 (4·90) per cent.]. $C_6H_4O_3NNa,2H_2O$, orange-red, microscopic needles [Found: N = 6·97 (7·11); Na = 11·81 (11·67); H_2O = 18·72 (18·28) per cent.]. $C_6H_4O_3NNa$, dark orange-red [Found: N = 8·53 (8·70); Na = 14·45 (14·28) per cent.]. $C_6H_4O_3NK,2H_2O$, flat, short, orange needles [Found: N = 6·77 (6·57); K = 18·04 (18·34); H_2O = 16·26 (16·90) per cent.]. $2C_6H_4O_3NK,C_6H_5O_3N,2H_2O$, pale orange granules [Found: N = 7·80 (7·96); K = 14·65, 14·86 (14·77); H_2O = 6·86 (6·81) per cent.]. $C_6H_4O_3NK$, deep orange [Found: N = 8·00 (7·91); K = 21·71 (22·07) per cent.]. $C_6H_4O_3NRb,2H_2O$, brownish-orange-yellow, microscopic needles, becoming deep orange in carbon tetrachloride, melting to a blood red liquid in boiling toluene, and giving a colourless solution in hot ethyl acetate [Found: N = 5·34 (5·37); Rb = 32·93 (32·93); H_2O = 13·09 (13·88) per cent.]. $C_6H_4O_3NRb$, deep orange-red [Found: N = 6·14 (6·27); Rb = 37·62 (38·23) per cent.]. $C_6H_4O_3NCs,H_2O$, red rosettes of needles, unstable in air, becoming orange, melting to a blood red liquid in toluene, giving a deep orange solution in alcohol, and becoming pale yellow in ethyl acetate [Found: N = 5·15 (4·85); Cs = 45·59 (45·98); H_2O = 6·37 (6·23) per cent.]. $C_6H_4O_3NCs$, deep orange-red [Found: N = 5·19 (5·17) per cent.].

Derivatives of p-*Nitrophenol.*—$2C_6H_4O_3NLi,C_6H_5O_3N,4H_2O$, yellow plates [Found: N = 7·98 (8·39); Li = 2·65 (2·77); $C_6H_5O_3N + H_2O$ = 41·31 (42·23) per cent.]. $C_6H_4O_3NLi$, orange-yellow [Found: N = 9·93 (9·89); Li = 4·28 (4·90) per cent.]. $C_6H_4O_3NNa,2H_2O$, brilliant yellow needles [Found: N = 7·15, 7·18 (7·11); Na = 11·75, 11·63 (11·67); H_2O = 17·89, 18·35, 17·95 (18·28) per cent.]. $2C_6H_4O_3NNa,H_2O$, orange, becoming yellow in alcohol, ether, or acetone and red in hot pyridine. Further exposure of this hydrate yields the hydrated form (+ $2H_2O$) [Found: N = 8·40 (8·24); Na = 13·11 (13·52); H_2O = 5·17 (5·29) per cent.]. $C_6H_4O_3NNa$, scarlet modification, becomes yellow in ether or alcohol and orange in acetone [Found: N = 8·50 (8·70); Na = 14·31 (14·28) per cent.]. $C_6H_4O_3NNa$, yellow form [Found: Na = 14·28 (14·28) per cent.]. $C_6H_4O_3NK,H_2O$, golden-yellow granules [Found: N = 6·98 (7·18); K = 20·48 (20·03); H_2O = 9·14 (9·23) per cent.]. $C_6H_4O_3NK$, deep yellow [Found: N = 7·89 (7·91); K = 22·72 (22·07) per cent.]. $C_6H_4O_3NRb,H_2O$, orange-yellow, microscopic needles, becoming deep yellow in toluene or pyridine [Found: N = 5·90 (5·80); Rb = 35·69 (35·30); H_2O = 7·41 (7·46) per cent.]. $C_6H_4O_3NRb$, deep yellow [Found: N = 6·37 (6·27); Rb = 38·50 (38·23) per cent.]. $C_6H_4O_3NCs,H_2O$, lemon-

yellow needles, becoming deeper yellow in pyridine, toluene, or ethyl acetate [Found: N = 4·87 (4·85); H_2O = 6·33 (6·23) per cent.]. $C_6H_4O_3NCs$, deep yellow [Found: N = 5·27 (5·17) per cent.].

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XII.—*Physical Chemistry of the Oxides of Lead. Part III. Hydrated Lead Monoxide.*

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THE true hydroxide of bivalent lead, $Pb(OH)_2$, has not yet been isolated, but two hydrated oxides, having the formulæ $3PbO,H_2O$ and $2PbO,H_2O$ respectively, have been reported. A repetition of the methods of preparation described by previous authors failed to yield any product which could be described as either of these two compounds; in almost every case analysis gave results intermediate between those required for the two hydrated oxides. The object of this work was to find the composition and structure of the substances actually obtained. The methods of preparation were as follows :—

I. *Methods supposed to give the compound* $2PbO,H_2O$.—(*a*) Schaffner (*Annalen*, 1844, **51**, 175). Lead acetate solution was treated with a slight excess of potassium hydroxide solution; the product appeared to be amorphous.

(*b*) Luedeking (*Amer. Chem. J.*, 1891, **13**, 120).—A solution of lead monoxide in sodium hydroxide solution was exposed to the carbon dioxide of the air. Highly refracting crystals slowly formed.

II. *Methods supposed to give the compound* $3PbO,H_2O$.—(*a*) Payen (*Ann. Chim. Phys.*, 1866, [iv], **8**, 302). The success of this method depends on a fairly definite concentration of ammonia. As the quantities given by Payen are rather vague, the following method was worked out. To 50 c.c. of a cold saturated solution of basic lead acetate (made by boiling lead acetate solution with excess of lead monoxide) a mixture of 45 c.c. of distilled water and 5 c.c. of ammonia solution ($d^{15°}$ 0·880) was added. The whole was kept for twenty-four hours at room temperature in a clean stoppered bottle. Highly refracting crystals formed on the sides and bottom of the bottle.

(*b*) Mulder (*J. pr. Chem.*, 1879, [ii], **19**, 79). This reference, although given in several text-books, could not be traced; the details are taken from Dammer, "Anorganische Chemie," II, 2, p. 524. A solution of a lead salt was treated with an alkali hydroxide solution, the clear liquor was decanted off, and the precipitate boiled

with more alkali. As boiling with alkali converts the hydroxide into lead monoxide, this method is uncertain.

(*c*) Ditte (*Compt. rend.*, 1882, **94**, 1310). Lead hydroxide, to which is given the formula $Pb(OH)_2$, freshly precipitated by alkali, is said to be converted into $3PbO,H_2O$ by digestion with 40 per cent. potassium hydroxide solution at 15°. This result could not be confirmed; the freshly precipitated product, when digested with alkali, washed, and dried in a vacuum, gave a product identical with that obtained by washing and drying the original hydroxide. That no change takes place during drying is shown by the fact that the freshly precipitated and dried forms have equal solubilities (see below).

Ditte's second method was to saturate 10 to 30 per cent. potassium hydroxide solution with lead hydroxide at a high temperature (insufficient to dehydrate the latter), and to allow to cool. In practice, this procedure was found to give green lead monoxide; the cold solution on exposure to the air slowly deposited crystals (compare Luedeking, *loc. cit.*).

(*d*) Pleissner (*Arb. Kaiser. Gesundh.-Amt.*, 1907, **26**, 384). Thirty-six c.c. of 16 per cent. lead acetate solution were added to 150 c.c. of 4 per cent. baryta solution in the cold. The precipitate, dried to constant weight over sulphuric acid, gave on analysis (by Pleissner) Pb = 89·5; H_2O = 3·18 per cent. (0·41 per cent. missing).

Böttger (*Z. physikal. Chem.*, 1903, **46**, 580) added lead acetate solution to baryta in the cold and obtained a product to which he ascribed the formula $5PbO,3H_2O$.

III. *Other Methods.*—(*a*) Lorenz (*Z. anorg. Chem.*, 1897, **12**, 436) electrolysed a solution of sodium nitrate, using a lead anode and a platinum cathode, and stated that a hydrated oxide of lead was produced. This method, however, was found always to yield a basic nitrate.

(*b*) Böttger (*loc. cit.*) made various compounds, supposed to be hydrated oxides, by the action of ammonium hydroxide on lead acetate solution, and of lead nitrate solution on baryta water. These products, however, were all found to be basic salts.

(*c*) Wood (T., 1910, **97**, 878) prepared a "hydroxide" by the action of ammonium hydroxide on lead nitrate solution. A number of attempts, with varying concentrations of the reactants, always gave basic nitrate.

(*d*) Winkelblech (*Annalen*, 1837, **21**, 21) and Schaffner (*loc. cit.*) stated that with lead nitrate solution and alkali hydroxides only basic salts are obtained. It has been found, however, that if the precipitate is repeatedly digested with sodium hydroxide solution, a hydrated oxide may be obtained free from basic salt.

Preparations made by the above methods were well washed and dried in a vacuum over calcium chloride. The amount of water in each product was estimated by heating a weighed quantity of the hydrated oxide to incipient fusion of the lead oxide formed and then rapidly cooling; in this way any red lead or carbonate formed during the initial gradual heating was decomposed. Winkelblech (*loc. cit.*) had noted that lead hydroxide kept at 105° lost 0·6 per cent. of water before decomposition set in; this result has been confirmed. Various products were kept at 105—110°, and a current of dry air, free from carbon dioxide, was passed over them; as soon as decomposition commenced (noted by slight colour change) the products were cooled and the water content was estimated. $3PbO,H_2O$ requires H_2O = 2·62 per cent.; $2PbO,H_2O$ requires H_2O = 3·88 per cent.

Results.

Method.	Reported to give	Found : H_2O per cent.	Decomposes when the percentage of water is
I (*a*)	$2PbO,H_2O$	(See below)	(varies with the conditions)
I (*b*)	,,	3·10	3·08
II (*a*)	$3PbO,H_2O$	3·09	3·00
II (*b*)	,,	(See below)	
II (*c*)	,,	3·75	3·13
II (*d*)	$3PbO,H_2O$ (Pleissner) $5PbO,3H_2O$ (Böttger)	3·50	3·10
III (*a*)	Hydrated oxide	(Basic nitrate)	
III (*b*)	$4PbO,5H_2O$	,, ,,	
III (*c*)	Hydrated oxide	,, ,,	
III (*d*)	Basic nitrate	3·79	

By the action of alkali on lead acetate solution, Schaffner (*loc. cit.*) and Mulder (*loc. cit.*) obtained what were supposed to be different products; further, Dammer (*op. cit.*) states that Mitscherlich (no reference given) obtained in this way a substance containing 3·50 per cent. of water. It seemed worth while to investigate the composition of the hydrated oxide produced under varying conditions of temperature and concentration. Solutions of sodium hydroxide at a known temperature were added to solutions of lead acetate; the products were filtered, washed, and dried in a vacuum. The moisture content was estimated in each case.

Lead acetate solution.		Sodium hydroxide solution.			
C.c.	Molar conc.	C.c.	Molar conc.	Temp.	H_2O per cent.
100	0·5	100	2·5	20°	3·75
100	0·9	50	10·0	,,	3·96
150	0·2	150	0·5	,,	3·70
200	0·05	75	0·5	,,	(Hydroxide mixed with oxide).
100	0·5	100	2·5	60	3·48
100	0·5	100	2·5	80	3·17
150	0·2	200	0·4	,,	(Hydroxide mixed with oxide).
150	0·2	200	0·4	70	3·09

The composition of the hydrated oxide thus depends on the temperature and the concentration of the reacting solutions; the higher the temperature and the greater the dilution, the lower is the water content. When the dried products were heated in a current of air, decomposition began at almost identical points, namely, when the water content was 3·08—3·13 per cent. It is possible that all these products are identical, the difference being due to varying amounts of adsorbed water; the latter would depend on the temperature and concentration of the precipitants.

In no case so far examined has any hydrated oxide been obtained (whether crystalline or amorphous) which can be said definitely to have the formula $3PbO,H_2O$ or $2PbO,H_2O$. We will first examine the case of the crystalline forms, namely, I (*b*) and II (*a*). There are three possible explanations: (1) the crystals formed are pure substances with the formula $8PbO,3H_2O$ (requires H_2O = 2·94 per cent.) or $5PbO,2H_2O$ (requires H_2O = 3·18 per cent.); (2) the substances are mixed crystals of the two hydrated oxides; and (3) the crystals consist of the compound $3PbO,H_2O$ with 0·5 per cent. of adsorbed water. The last possibility was tested by keeping some ground crystals at 70° for three weeks in a vessel connected with a phosphoric oxide bulb under a vacuum of 1 mm. of mercury. It was thought that under these conditions adsorbed water would be removed; a very small loss actually occurred, *but slight dehydration accounted for this.* The choice is thus between the first two explanations, but there appears to be no means of deciding which is correct.

In the case of the amorphous products, where the water content varied between 3·96 and 3·09 per cent., three explanations are possible. The products may be (1) mixtures of the two hydrated oxides, (2) the compound $3PbO,H_2O$ together with more or less adsorbed water, or (3) solid solutions of the compounds $3PbO,H_2O$ and $2PbO,H_2O$, with or without adsorbed water. In case (1) a solvent should effect a partial separation, and the attempt was made with sodium hydroxide solution. Products containing 3·75 and 3·48 per cent. of water respectively were shaken for several weeks with sufficient 10 per cent. sodium hydroxide solution to dissolve half the solid (6 grams of hydrated oxide to 100 c.c. of alkali); the residue was filtered off, washed, and dried. In neither case did the final product at all differ from the original substance. We are thus not dealing with an ordinary two-phase mixture.

Every preparation of hydrated lead oxide examined lost water on heating until decomposition set in at a point which was almost identical in each case (3·08 to 3·13 per cent. of water). From this it seems that we are dealing, in every form of hydrated oxide,

whether crystalline or amorphous, with the same chemical entity together with varying amounts of adsorbed water. Whether this substance is a single compound or a solid solution of two or more substances, it seems impossible to decide. In the latter case we should expect products prepared at different temperatures to vary somewhat in composition; the actual variations found (see above) are too small to be ascribed to any definite cause.

Solubility in Sodium Hydroxide.

Rubenbauer (*Z. anorg. Chem.*, 1902, **30**, 331) made a series of solubility measurements on a hydrated oxide prepared by Schaffner's method (*loc. cit.*). Wood (*loc. cit.*), in his solubility measurements, employed what was probably a basic nitrate; this would have a solubility in alkali almost identical with that of the hydrated oxide, provided that allowance were made for the alkali used up in decomposing the basic salt. The error caused by the omission of this correction would be comparatively greater in the more dilute solutions. Pleissner (*loc. cit.*) has made a study of the hydrated oxide II (*d*), and has determined its solubility in water by chemical methods. It was considered desirable to use this product for solubility determinations in varying concentrations of sodium hydroxide solution.

Sodium hydroxide solutions (free from carbonate) were shaken with quantities of the hydrated oxide in stoppered bottles, which were then placed in a thermostat at 25°. Portions of the clear liquids were withdrawn from time to time and analysed, until constant values were obtained. The method of analysis was that given in Part I (T., 1921, **119**, 1689).

All concentrations are expressed in gram-mol. per litre at 25°.

Conc. of NaOH.	PbO,xH_2O *in* solution.	*Sodium* plumbite.	*Residual* NaOH.	$\frac{[HPbO_2']}{[OH']} = k$	$\frac{PbO,xH_2O}{PbO}$
0·9985	0·0620	0·06155	0·9370	0·0657	1·78
0·7489	0·0484	0·04795	0·7010	0·0684	
0·4993	0·0345	0·03405	0·4653	0·0732	1·77
0·2496	0·0178	0·01735	0·2323	0·0747	
0·1177	0·00881	0·00836	0·1093	0·0765	1·74
0·0499	0·00392	0·00347	0·0464	0·0748	1·70

These figures were obtained by the method described in Part I (*loc. cit.*) on the assumption that the hydrated oxide dissolves in sodium hydroxide according to the equation

$$PbO,xH_2O + OH' \rightleftharpoons HPbO_2' + xH_2O.$$

The solubility of the hydrated oxide in water was taken as $0{\cdot}45 \times 10^{-3}$ gram-mol. per litre (Pleissner, *loc. cit.*). The last column shows

the ratio of the solubilities of hydrated oxide and anhydrous oxide in alkali of the same concentration. By means of the method previously described the dissociation constant of the monobasic acid $H\cdot HPbO_2$ produced by dissolving hydrated lead oxide in water is calculated as $1\cdot35 \times 10^{-12}$ at 25°.

Solubility in Potassium Hydroxide.

Herz (*Z. anorg. Chem.*, 1901, **28**, 475) determined the solubility of lead "hydroxide" in potassium hydroxide solution at the ordinary temperature by two methods: (*a*) alkali solution of known concentration was added to a standard lead solution until the precipitate just redissolved, and (*b*) hydrated oxide prepared by the action of alkali on lead acetate solution was dried at 60°, and shaken with potassium hydroxide solution for one hundred hours. The results in each case indicated that 1 gram-mol. of lead hydroxide requires 8·5 to 8·8 gram-equivs. of hydroxyl ions for dissolution. Rubenbauer (*loc. cit.*) remarked on the apparent difference between sodium and potassium hydroxides, as in the former case about 15 gram-equivs. are necessary to dissolve 1 gram-mol. of the hydrated oxide. The results of Wood (*loc. cit.*) as well as those given above confirm the measurements of Rubenbauer, but a repetition of Herz's experiments failed to yield results in accordance with those given.

(1) Twenty c.c. of a solution containing 1·184 grams of lead acetate in 250 c.c. of water required 42 c.c. of $N/10$-potassium hydroxide completely to dissolve the precipitate. Allowing for the potassium hydroxide required to convert the acetate into hydroxide, we find that 1 gram-mol. of the hydrated oxide requires 14·8 gram-equivs. of alkali for dissolution.

(2) Solubility determinations according to Herz's second method gave the following results:

Concentration of KOH.	PbO,xH_2O. Gram-mol. per litre.	$\frac{KOH}{PbO,xH_2O}$.	$\frac{NaOH}{PbO,xH_2O}$.
0·9985 N	0·0631	15·8	16·1
0·1177 N	0·00892	13·2	13·4

The value of the ratio of sodium hydroxide to hydrated lead oxide is added for the sake of comparison. The anomaly in the case of potassium hydroxide is thus probably due to erroneous results.

Potential Measurements.

The potential of the half-element Pb | PbO,xH_2O N-NaOH was determined by reference to the Hg | HgO N-NaOH electrode. With

all the forms of hydrated oxide prepared, the value of the potential was $-0{\cdot}554$ volt at 20°, the corresponding potential with lead monoxide being $-0{\cdot}559$ volt. The free energy of the reversible change

$$PbO,xH_2O \rightleftharpoons PbO + xH_2O,$$

with the water at the aqueous-vapour pressure of *N*-sodium hydroxide at 20°, is thus $0{\cdot}005 \times 2 \times 96540$ joules per gram-mol. of lead monoxide, the hydrated oxide being metastable with respect to the oxide. The relative stability is also clear from the solubility determinations, and from the observed change of hydrated oxide to oxide in the presence of alkali or boiling water (compare Pleissner, *loc. cit.*).

Aqueous-vapour Pressure of the Hydrated Oxide.

If the vapour pressure of *N*-sodium hydroxide is taken as 15 mm. of mercury, the aqueous-vapour pressure, p mm., of the hydrated oxide is given by the equation :

$$\log p = \frac{1}{x} \cdot \frac{0{\cdot}005}{0{\cdot}029} + \log 15.$$

Putting $x = 1$, for $Pb(OH)_2$, p is calculated as 22 mm.; if $x = 1/2$, for $2PbO,H_2O$, p is 33 mm.; and if $x = 1/3$, for $3PbO,H_2O$, then p is 49 mm. Experimental determinations of the aqueous-vapour pressure of partly decomposed hydrated oxide by the Cumming method (T., 1909, **95**, 1772) and by the use of the Frowein tensimeter failed to indicate any appreciable vapour pressure at room temperature. The fact that the hydrated oxide does not lose weight in a vacuum desiccator confirms this absence of vapour pressure. The high values calculated above were obtained on the assumption that the *reversible* reaction

$$\text{Hydrated oxide} \rightleftharpoons \text{Anhydrous oxide} + \text{Water vapour}$$

is capable of experimental realisation. We may be dealing with a case of suspended transformation, but this appears scarcely likely, since the products used for measurement were partly decomposed by heat. An alternative possibility is that the " hydrated oxide " is not a hydrated oxide or hydroxide in the ordinary sense in which these terms would be employed. In this case a reversible dissociation with the formation of lead monoxide and water vapour would not necessarily follow, although thermodynamically there would be an ultimate tendency for such decomposition to take place. It is suggested that the hydrated oxides may be salts of the monobasic

acid, $H\cdot HPbO_2$, allied to formic acid. Thus lead plumbite would be $Pb(HPbO_2)_2$, that is, $3PbO,H_2O$, whilst a basic salt would be $Pb(OH)(HPbO_2)$, that is, $2PbO,H_2O$. In solution, these salts would be in equilibrium with true hydroxide owing to hydrolysis, and therefore would exhibit the metastability with regard to the oxide indicated by solubility and *E.M.F.* measurements, and yet would exert no appreciable vapour pressure in the solid state.

It should be possible to prepare other plumbites having the formulæ $M^{I}(PbO\cdot OH)$ or $M^{II}(PbO\cdot OH)_2$, in both cases apparently containing molecules of water, yet not necessarily having any appreciable vapour pressure. Wöhler (*Pogg. Annalen*, 1837, **41**, 344) added sodium hydroxide solution to a mixed solution of lead and silver nitrates, and obtained a yellow precipitate which was estimated to contain 34·23 per cent. of silver oxide and 65·77 per cent. of lead oxide. Owing to the indefinite state of the knowledge of atomic weight and valency at that time little importance can be attached to these results. Krutwig (*Ber.*, 1882, **12**, 1264) modified Wöhler's method by adding alkali to the lead nitrate solution until the precipitate redissolved, and then adding silver nitrate solution. The yellow precipitate was washed with boiling alkali solution and with hot water. The analysis of the product (dried in a vacuum) agreed with the formula $Ag_2PbO_2,2H_2O$. In giving this formula, Krutwig was probably influenced by the belief current at the time, that H_2PbO_2 was a dibasic acid—an assumption not in agreement with later work. Preparations made according to these two methods were amorphous, and of similar but uncertain composition. The average of a number of analyses gave a ratio of 2·3 gram-mols. of lead monoxide to 2·0 gram-mols. of silver oxide and 1·0 gram.-mol. of water, corresponding roughly with the formula $(Ag\cdot HPbO_2)_2,Ag_2O$. This formula is of the same type as that of the basic salts of ethylstannous acid (wrongly called ethylstannic acid) prepared by Druce (T., 1921, **119**, 758). This acid also gave a number of normal salts (the ethyl group probably increasing the strength of the acid), and an attempt is being made to prepare similar salts of ethyl- and methyl-plumbous acid. The silver plumbite prepared resembled hydrated lead oxide in having no appreciable aqueous-vapour pressure and in losing water on gentle heating, yielding a mixture of lead and silver oxides. Boiling water or hot alkali hydrolysed the salt, giving lead oxide, which dissolved in the alkali, leaving black silver oxide. Attempts made to prepare plumbites of tin, copper, and mercury failed to yield any definite products containing both lead and the other metal; in the case of mercury a brown powder was obtained which contained about 10—12 per cent. of lead.

Summary.

(1) No method of preparation hitherto described yields a substance which has definitely the composition $3PbO,H_2O$ or $2PbO,H_2O$; the actual products are either pure substances of the formula $5PbO,2H_2O$ or $8PbO,3H_2O$, or solid solutions of two or more simple hydrated oxides.

(2) The composition of the material obtained by precipitating a lead salt solution with alkali depends on the temperature and concentration of the precipitants; this is probably due to variation in the amount of adsorbed water.

(3) The dissociation constant of the monobasic acid, $H{\cdot}HPbO_2$, produced by dissolving the hydrated oxide in water is $1{\cdot}35 \times 10^{-12}$ at 25°.

(4) Many of the chemical and physical properties of the so-called hydrated oxide may be readily explained by assuming that the substance is a lead plumbite.

The author's thanks are again due to Professor Allmand for suggestions and criticism.

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XIII.—*Occurrence of a Crystalline Tannin in the Leaves of the* Acer ginnala.

By ARTHUR GEORGE PERKIN and YOSHISUKE UYEDA.

THE *Acer ginnala*, or Korean maple tree, is common throughout Korea, and is especially prolific at the boundary between that country and China. The shrubs average from 3 to 4 feet, although occasionally reaching 8 to 9 feet in height, and the leaves are of service on account of the tannin matter they contain. As a rule, the latter are plucked during mid autumn, about 1 lb. being yielded by each plant, and in the dried condition, admixed with the small twigs, they are exported to China. In that country they are employed extensively for the black dyeing of cotton, natural copperas affording the mordant, and in 1917 the amount sent there, according to the Custom House authorities, was about two million kin, equivalent to 2,650,000 English pounds. The price averaged three yen, or six shillings per 100 lb.

On behalf of the Government of Korea, a preliminary investigation of this material was carried out in that country by one of us (Uyeda) at the Central Experimental Station (*J. Chem. Ind. Tokyo*, 1918, **21**, 211; *J. Soc. Chem. Ind.*, 1918, **37**, 412). As a result of this, an extract of the leaves is now prepared [termed Shinnama (bitter tree) extract] containing about 30 per cent. of tannin, and this is used in Japan for cotton and silk black dyeing with iron mordant and for the production of a khaki shade on chrome-mordanted wool (Kogyo Kwagaku-Zasshi).

The present work was instituted in order to obtain information as to the chemical nature of both the yellow colouring and tannin matters present in the leaves.

EXPERIMENTAL.

Five hundred grams of the air-dried leaves of the *Acer ginnala* were extracted twice with 3 litres of boiling absolute alcohol for three hours, and the combined extracts concentrated to about 200 c.c. Water (250 c.c.) was now added, the alcohol boiled off, and the mixture freed from chlorophyll and wax by means of commercial ether (*A*), some tannin being simultaneously removed. To the aqueous liquid freed from ether 15 grams of sodium hydrogen carbonate were added, and after a short treatment with carbonic acid gas the solution was agitated six times with ethyl acetate or until the tannin was no longer removed thereby. The latter extracts, after agitation with sodium chloride and filtration, were evaporated to dryness under reduced pressure and gave a pale yellow, puffed-up mass resembling gallotannin, which weighed 36·9 grams.

This product, treated with twice its volume of warm water, passed mainly into solution, but, on boiling, the mixture became semi-solid owing to the separation of crystals. When cold, these were collected and washed with water, the pale brown filtrate (*B*) being reserved for subsequent examination. The crystals, which averaged, when dry, 60 per cent. of the crude tannin, were recrystallised two or three times from about 30 parts of boiling water.*

From the ethereal liquid *A*, by agitation with water and treatment of the washings by the process just described, a further 8·7 grams of

* The tannin can also be obtained, but in a somewhat less pure form, from the solid commercial extract of the leaves manufactured in Korea. This is digested with alcohol and the alcoholic liquid worked up as stated above. The yield of crude tannin thus obtained averages 15·5 per cent. Some gallic acid is also present in the ethereal extract.

the tannin could be isolated, giving a total yield of 45·6 grams. The latter product, however, contained a little chlorophyll, to remove which a short digestion with boiling benzene was necessary. The pure tannin, crystallised from water, consisted of colourless, prismatic needles which melted at 164—166°. Air-dried, it did not lose water of crystallisation at 100° (Found : C = 47·52; H = 4·85. $C_{20}H_{20}O_{13},2H_2O$ requires C = 47·61; H = 4·76 per cent.).

Heated at 125° for several hours, one molecule of water was evolved (Found : H_2O = 3·65. Calc., H_2O = 3·57 per cent. Found : in the residual substance, C = 49·56; H = 4·44. $C_{20}H_{20}O_{13},H_2O$ requires C = 49·39; H = 4·52 per cent.).

Finally, at 140°, the air-dried substance evolved two molecules of water (Found : H_2O = 6·95. Calc., H_2O = 7·14 per cent. Found : in the anhydrous substance, C = 51·07; H = 4·31. $C_{20}H_{20}O_{13}$ requires C = 51·28; H = 4·28 per cent.).

When dried at 140°, the product is hygroscopic, and on standing in air regains in a short time its original weight. On keeping, however, over-night, curiously enough, a further gain equivalent to a molecule of water occurs, the total amount approximating to $3H_2O$ (Found : H_2O = 10·75. Calc., H_2O = 10·35 per cent.).

If acertannin (1 gram) is dissolved in boiling 50 per cent. alcohol and the solution is not agitated,* it slowly separates as prisms usually possessing a faint brown tint. These, which congeal as the crystallisation proceeds, are difficult to obtain free from the needle variety. Two distinct preparations thus obtained, when heated at 100°, became colourless and opaque, and lost 3½ molecules of water of crystallisation (Found : H_2O = 11·41, 11·66 per cent.). At 125° four molecules were evolved (Found : H_2O = 13·00, 13·12 per cent.), whereas at 140° no further loss was experienced ($C_{20}H_{20}O_{13},4H_2O$ requires H_2O = 13·3 per cent.).

Finally, the prism variety, dried at 140°, gave C = 51·48; H = 4·12 per cent. It thus seems evident that acertannin crystallises in two varieties, prismatic needles, $C_{20}H_{20}O_{13},2H_2O$, and prisms, $C_{20}H_{20}O_{13},4H_2O$. By heating to 140°, neither preparation undergoes decomposition and the melting point, 164—166°, is thereby unaltered.

Acertannin is very slightly soluble in cold water (approx. 0·2 per cent.), sparingly soluble in boiling water, of which about 30 parts are necessary for its solution, is readily soluble in alcohol, but slightly soluble in cold pure acetone, and gives with aqueous lead acetate and ferric chloride solutions respectively a colourless

* It is preferable to seed the warm solution with a crystal from a preceding preparation.

precipitate and a deep blue coloration. It possesses a slight astringent taste, not nearly so marked as that of gallotannin, and dissolves in dilute alkali with a pale yellow colour which becomes a deep brown-orange on exposure to air. With potassium acetate in absolute alcohol, it gives a thick, curdy precipitate, evidently of the potassium salt, which resinifies on standing, a reaction which is also exhibited by gallotannin and other synthetical tannins. A 0·4 per cent. solution gives with 1 per cent. gelatin in 10 per cent. sodium chloride solution an immediate precipitate, and this occurs as readily as with Kahlbaum's pure gallotannin. Like the latter, it also precipitates basic dyestuffs. It dissolves in sulphuric acid to form an almost colourless solution, which on warming becomes deep black, a property which is evidence of a sugar or carbohydrate nucleus. With potassium cyanide, no coloration is produced. Acertannin is optically active: 0·1147 gram in 20 c.c. of acetone gave $[\alpha]_D^{15^\circ} + 20 \cdot 55^\circ$.

The acid dissociation constant, kindly determined for us by Mr. W. R. Atkin, is 1×10^{-7}, which is practically identical with that of gallotannin.

Acetylacertannin.—Acertannin (2 grams) was acetylated by means of cold pyridine (6 c.c.) and acetic anhydride (6·5 c.c.) according to Fischer and Bergmann's method (*Ber.*, 1918, **51**, 1797). The acetyl compound thus obtained was crystallised from methyl alcohol, the operation being performed rapidly. It thus separated as ball-like masses of minute, colourless needles melting at 154—155°. From a very concentrated solution in hot methyl alcohol it was deposited, on cooling, as viscid globules [Found: C = 53·86; H = 4·22; acetic acid = 59·86. $C_{20}H_{12}O_{13}(C_2H_3O)_8$ requires C = 53·73; H = 4·47; acetic acid = 59·7 per cent.].

The acetyl estimation was carried out by the acetic ether method. Fischer and Bergmann (*loc. cit.*) have pointed out that in the case of acetyltannins prolonged contact with boiling alcohol during the crystallisation process results in a partial removal of the acetyl group. Acetylacertannin was observed to possess this property, for after a third crystallisation from methyl alcohol analysis gave acetic acid = 58·6 per cent. A molecular-weight determination of this substance was carried out by the cryoscopic method:

0·8197 in 12·09 of naphthalene gave $\Delta t = 0 \cdot 52^\circ$, whence $M = 785$. $C_{36}H_{36}O_{21}$ requires $M = 804$.

Hydrolysis of the Tannin Matter.—It was ascertained by preliminary experiment that acertannin is not readily hydrolysed by boiling with dilute sulphuric acid, although less resistant than gallotannin (Fischer and Freudenberg, *loc. cit.*) in this respect, and the following procedure was eventually adopted. Three grams of the tannin

$C_{20}H_{20}O_{13},2H_2O$ in 150 c.c. of 5 per cent. sulphuric acid were heated on the water-bath for twenty hours, causing the formation of a brown liquid, from which nothing separated on cooling over-night. The solution was extracted ten times with ethyl acetate, the extract agitated with sodium chloride, and evaporated to dryness, thus yielding a pale brown, crystalline mass, 1·949 grams. This, after a recrystallisation from water, melted at 238—242° with effervescence, and without doubt consisted of gallic acid.

In order to isolate the sugar from the residual liquid and to remove completely therefrom the last traces of gallic acid and a brown impurity still present, only the method given by Fischer and Freudenberg in the case of gallotannin (*loc. cit.*) proved effective. There was thus obtained a pale brown, viscid mass, which was digested with boiling absolute alcohol. After filtration from a trace of mineral matter, the solution, on partial evaporation and keeping during several days, gradually deposited colourless crystals. These, when dry, weighed 0·6 gram, and from the mother-liquor, by evaporation, 0·0715 gram was further obtained. This small yield of sugar is accounted for, no doubt, by its partial destruction during the prolonged action of the dilute sulphuric acid; such destruction has been shown to occur, although in a less marked degree, in the case of the glucose liberated during hydrolysis of gallotannin. The total weight of crude gallic acid isolated by these methods was 64·99 per cent. by weight, whereas in case the molecule $C_{20}H_{20}O_{13},2H_2O$ contained two galloyl nuclei the yield should be 67·46 per cent. The sugar thus obtained melted at 141—142° and, after one recrystallisation from alcohol, at 142—143° (Found: C = 44·13; H = 7·43. $C_6H_{12}O_5$ requires C = 43·90; H = 7·31 per cent.).

This compound, for which the name *aceritol* is proposed, crystallises from alcohol, in which it is moderately soluble, in small, colourless prisms, whereas by solution in 6 parts of hot water and keeping in a vacuum desiccator crystals of a considerable size are obtained (Found: C = 44·02; H = 7·2 per cent.).

We are much indebted to Miss M. W. Porter of Oxford for their examination.

The system is monoclinic, with $a : b : c = 0·8334 : 1 : 0·5692$; $\beta = 109° 59'$. Forms: $b\{010\}$, $a\{100\}$, $m\{110\}$, $c\{001\}$, $q\{011\}$. The crystals exhibit two distinct habits, as shown in Figures 1 and 2. Two crystals were measured and the results are given in the table below.

	$b\{010\}$.	$a\{100\}$.	$m\{110\}$.	$c\{001\}$.	$q\{011\}$.
ϕ ...	0° 34′ (−34′)	90° 2′ (−2′)	51° 56′*	88° 51′ (+1° 9′)	32° 53′ (−18′)
ρ ...	89 57 (+3′)	89 58 (+2′)	89 59 (+1′)	19 59*	34 2*

Optic axial plane $b\{010\}$; the negative acute bisectrix is almost perpendicular to $c\{001\}$. The axial angle is wide and the double refraction strong. Dispersion $\rho < v$.

FIG. 1.

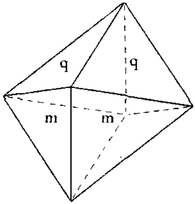
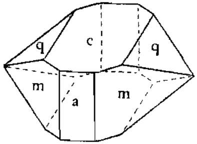


FIG. 2.



Heated in a test-tube, aceritol distils almost without carbonisation very similarly to mannitol, giving a colourless distillate which, on cooling, forms a glossy mass. With phenylhydrazine, no osazone has yet been obtained from it under conditions which readily gave the osazone of glucose and galactose, and when it was distilled with hydrochloric acid in the usual manner the presence of furfuraldehyde or methylfurfuraldehyde could not be detected. It does not reduce Fehling's solution, and when digested with dilute hydrochloric acid and resorcinol does not give the red coloration which is an indication of a keto-hexose.

Aceritol is dextrorotatory, a 1 per cent. aqueous solution giving $[\alpha]_D^{19°} + 39°$.*

For acetylation, it was boiled for ten minutes with 2 parts of acetic anhydride containing a trace of zinc chloride, the solution diluted with alcohol, evaporated, and the product treated in a similar manner. A solution of the viscid residue in methyl alcohol slowly deposited crystals, and these, after washing with water and dilute acetic acid, were recrystallised twice by means of benzene and light petroleum [Found: C = 50·86; H = 6·19; acetic acid = 72·41. $C_6H_8O_5(C_2H_3O)_4$ requires C = 50·6; H = 6·02; $C_2H_4O_2$ = 72·3 per cent.].

Tetra-acetylaceritol consists of long, fine needles melting at 74—75°, readily soluble in benzene or alcohol. That aceritol contains four hydroxyl groups is in harmony with the fact that acertannin yields an octa-acetyl compound and indicates that in this compound six acetyl groups are present in the galloyl nuclei and two in the sugar nucleus.

* Our thanks are due to Mr. A. Shimomura for this determination.

In order to determine if acertannin contained a digallic or a gallic acid residue, 2 grams of the dihydrate, $C_{20}H_{20}O_{13},2H_2O$, in 4 c.c. of acetone were methylated by means of a slight excess of diazomethane (compare Fischer and Freudenberg, *Ber.*, 1914, **47**, 2485). The solution, after keeping for some days, was evaporated under diminished pressure and thus yielded a viscid, almost colourless residue which did not become crystalline on keeping. It was hydrolysed by treating its solution in cold methyl alcohol with 15 c.c. of *N*-sodium hydroxide and allowing the mixture to remain at the ordinary temperature for three days. The liquid was now neutralised with dilute sulphuric acid and the alcohol removed by distillation. Colourless crystals thus separated (1·402 grams) and from the mother-liquor, by means of ether, 0·232 gram of crystals of a faintly brown colour and admixed with a little resinous matter was isolated. These products were entirely soluble in a mixture of equal volumes of carbon tetrachloride and chloroform, indicating the absence of gallic acid dimethyl ether (Fischer and Freudenberg, *loc. cit.*). After recrystallisation, both fractions melted at 170° and without doubt consisted of gallic acid trimethyl ether.

The weight of the crude product of the hydrolysis (1·634 grams or 81·7 per cent. approximately) corresponds nearly with the amount of gallic acid trimethyl ether which should be yielded by a digalloylaceritol, $C_{20}H_{20}O_{13},2H_2O$, namely, 84·1 per cent. As a result, it was apparent that a galloyl and not a digalloyl nucleus is present in acertannin.

Non-crystalline Tannin.

The brownish-yellow mother-liquors (*B*) obtained during the first crystallisation of the tannin were repeatedly extracted with ethyl acetate, and the extract was agitated with sodium chloride and evaporated to dryness under reduced pressure. The puffed-up mass thus obtained in amount equal to about 40 per cent. of the original crude tannin could not be crystallised, but separated from its concentrated solution, on keeping, as a viscid mass. The aqueous solution, acidified with a little acetic acid, gave with lead acetate a pale yellow deposit, this colour arising from the presence of a flavonol glucoside, but an attempt to remove the latter from the tannin by fractional precipitation was unsuccessful.

The lead precipitate, decomposed by hydrogen sulphide in the usual way, yielded a somewhat purer product resembling gallotannin in appearance, which gave with ferric chloride a greenish-blue coloration and readily precipitated gelatin solution. When it was hydrolysed with 5 per cent. sulphuric acid for twenty hours, a small amount of brown precipitate separated, a solution of which in

alcohol, when diluted with ether, gave a brown deposit resembling a catechol tannin phlobaphen, whereas the clear liquid contained a flavonol dyestuff which is dealt with later on. The main acid filtrate gave to ethyl acetate a large amount of gallic acid, and by subsequent treatment according to the method already described, a crystalline sugar identical with aceritol was isolated in fair quantity, although a more exhaustive purification was necessary in this case. It is accordingly evident that this non-crystalline tannin preparation consisted mainly of a galloyl- or galloyl-aceritols together with small amounts of a flavonol glucoside and a substance which is probably a phlobo (catechol) tannin.

Ellagic Acid.

The aqueous liquid from which the tannin had been removed by means of ethyl acetate contained a pale yellow, semi-crystalline precipitate. This product exhibited the reactions of ellagic acid, and to establish its identity it was acetylated with acetic anhydride (in the presence of sulphuric acid) and recrystallised from the same solvent (Found: C = 56·32; H = 3·19. $C_{22}H_{14}O_{12}$ requires C = 56·17; H = 2·98 per cent.).

The colourless tetra-acetyl compound sintered at 334° and melted at 340—342°, and when hydrolysed yielded pure ellagic acid.

The filtrate from the crude ellagic acid, by digestion at its boiling point with a little sulphuric acid, gave, on cooling, traces of ellagic acid and a flavone dyestuff, and there was also present some quantity of a brown precipitate resembling a catechol tannin phlobaphen.

The Yellow Colouring Matter.

The presence of such a dyestuff other than ellagic acid in the crude amorphous tannin has already been noted, and, again, it was known that the plant extract dyed mordanted calico pale yellow shades resembling those given by a flavone colouring matter. A boiling aqueous extract of the leaves (200 grams) was treated with lead acetate followed by a little ammonia. The bulky, pale yellow precipitate was collected, washed, and in the form of a thin cream decomposed with boiling dilute sulphuric acid. From the clear liquid, decanted while hot, the yellow colouring matter was isolated by means of ether, and this, after removal of the gallic acid also present, weighed 1·2 grams.

For purification it was dissolved in boiling alcohol, filtered from a trace of ellagic acid, and the solution cautiously diluted with boiling water. The fine, yellow needles which separated were

collected, washed with benzene, and acetylated in the usual manner [Found: C = 58·62; H = 3·85. $C_{15}H_5O_7(C_2H_3O)_5$ requires C = 58·59; H = 3·90 per cent.].

It was thus obtained as colourless needles melting at 191—195°, and this melting point remained unaltered when the substance was admixed with acetylquercetin. The yellow colouring matter of these leaves is therefore quercetin.

General Properties of the Leaf.

A comparison of the behaviour of an aqueous extract of the leaves of the *Acer ginnala* with that of sumach (*Rhus coriaria*) as an assistant for the fixation of basic dyes on cotton, indicated that the former was by far the less effective in this respect. Experiments, crystalline acertannin and the gallotannin of Kahlbaum again being employed, gave a like result, and it seems evident that this is due, at least in part, to the meagre affinity of acertannin for cotton.

An analysis of the air-dried leaf according to the official method of the Society of Leather Trades Chemists was kindly carried out for us by Professor McCandlish,

Tannin matter	14·5	per cent.
Soluble non-tannin matter	23·1	,,
Insoluble in cold water	51·3	,,
Water	11·1	,,

who reports that although a considerable amount of tannin matter is thus indicated, this is unsuitable for tanning purposes and by its action the hide is merely converted into a hard, brittle mass.* It thus seems certain that the *Acer ginnala* leaves are only of service for black dyeing purposes, the material being preferably first mordanted with iron. Laboratory experiments, employing cotton mordanted with iron in the usual manner, indicated that pure acertannin (5 per cent.) gives an excellent deep blue colour and by the employment of 10 per cent. a good black. It is evidently well suited also for the black dyeing of silk. The khaki colour given by the leaves on chrome-mordanted wool, which is referred to in the introduction, is due with little doubt to the ellagic acid and quercetin present rather than to the tannin itself.

* Comparative trials in this respect were also carried out with the bark of the *Hamamelis virginica*, which contains the crystalline digalloyl hexose (Freudenberg, *loc. cit.*) hamamelitannin. Although an analysis by the hide powder method indicated the presence of about 10 per cent. of tannin matter, the bark extract possessed but little tanning effect and yielded a product of the same character as, but slightly better than, that given by the leaves of the *Acer ginnala*.

Summary.

The leaves of the *Acer ginnala* are thus shown to yield a crystalline tannin, here termed acertannin, an amorphous tannin, some quantity of ellagic acid, a trace of quercetin, and apparently a small amount of a phlobo (catechol) tannin. Acertannin, $C_{20}H_{20}O_{13}$, crystallises in two forms, as needles with $2H_2O$ and as plates containing probably $4H_2O$, and yields a colourless, crystalline octa-acetyl compound. By hydrolysis with acid it yields 2 mols. of gallic acid and aceritol according to the following equation :

$$C_{20}H_{20}O_{13} + 2H_2O = 2C_7H_6O_5 + C_6H_{12}O_5,$$

and as the product of its methylation gives, when hydrolysed, gallic acid trimethyl ether only, it is evident that the two galloyl nuclei are separately attached to the " sugar " nucleus and that a digallic acid residue is absent. Althongh acertannin is not so resistant to acid as gallotannin (Fischer and Freudenberg, *Ber.*, 1912, **45**, 915), for which purpose hydrolysis for sixty to seventy hours with 5 per cent. sulphuric acid at 100° is necessary, it is sufficiently so to indicate, as would also be suggested hy its method of preparation, that it is not a glucoside–gallic acid such as the β-glucoside–gallic acid of Fischer and Bergmann (*Ber.*, 1918, **51**, 1804), but rather a sugar ester, as indeed is the case with gallotannin and the majority of natural tannins at present examined.

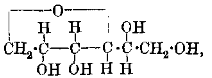
Acertannin is closely allied to hamamelitannin, which Freudenberg (*Ber.*, 1919, **52**, [*B*], 177) has shown to consist of a digalloyl hexose, and again is very similar to the digalloyl glucose which has been obtained hy Freudenherg and Fick from chebulinic acid (*Ber.*, 1920, **53**, [*B*], 1728).

The knowledge we now have of these compounds falls well into line with the classical researches of Fischer on gallotannin itself.

We are indebted to Professor Freudenberg for samples of these crystalline tannin matters, which, although resembling acertannin in appearance and general properties, are at once distinguished from it by their ready solubility in boiling water. Again, it was found that the more complex crystalline chebulinic acid prepared from myrabolans dissolves much more readily in boiling water than acertannin. That acertannin lacks real tanning properties, in which respect it resembles hamamelitannin, may arise from its paucity of galloyl groups or the lack of a digallic acid residue. Procter and Wilson (T., 1916, **109**, 1327), however, consider that vegetable tanning arises from the co-precipitation of oppositely charged colloids, whereas acertannin may not, like gallotannin, possess this colloidal character.

The dextrorotatory "sugar" aceritol, $C_6H_{12}O_5$, which yields a tetra-acetyl compound, possesses the properties of neither a ketose nor an aldose. Its behaviour when distilled resembles that of a polyhydric alcohol such as mannitol, and it is strongly suspected to consist of an anhydro-hexitol derived probably from either mannitol or sorbitol. It is common knowledge that polyhydric alcohols of this type form inner anhydrides, although these compounds, such as mannitan, have hitherto been obtained only as syrups, and it may be that aceritol is a definite anhydride of this class.

The properties of acertannin, $C_{20}H_{20}O_{13}$, and the fact that it yields aceritol with hot 5 per cent. sulphuric acid render it certain that this tannin matter is not in reality a digalloyl-hexitol, or that aceritol is formed by dehydration of the hexitol during hydrolysis. Evidently, however, the suggested anhydro-linking of aceritol which, in case it be derived from mannitol, may be thus expressed



is of a stable character, and hydrolysis to the hexitol may be difficult to accomplish.

We are indebted to Principal Irvine of St. Andrews University for suggestions as to likely methods of overcoming the difficulty, and these will form part of a further study of this interesting compound.

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XIV.—*The Direct Acetalisation of Aldehydes.*

By ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH.

THE researches of E. Fischer on the conversion of aldehydes into acetals by means of alcohol containing hydrogen chloride (*Ber.*, 1897, **30**, 3053; 1898, **31**, 345, 1989) suggested a close analogy between this process and the catalytic process for esterification of carboxylic acids. Delepine (*Compt. rend.*, 1900, **131**, 684, 745; 1901, **132**, 331, 969) showed that when aldehydes react with alcohols in presence of mineral acid an equilibrium is attained,

$$R{\cdot}CHO + 2R'{\cdot}OH \rightleftharpoons R{\cdot}CH(OR')_2 + H_2O,$$

the speed of reaction increasing with the proportion of mineral acid acting as catalyst. As the equation indicates, the proportion of acetal formed is detrimentally affected by the presence of water, and there can be little doubt that this factor is of predominating importance in the case of ketones, the acetals of which class cannot be prepared by Fischer's method.

The methods used by Claisen for the conversion of aldehydes and ketones into acetals (*Ber.*, 1893, **26**, 2731; 1896, **29**, 1005, 2931; 1900, **33**, 3778; 1903, **36**, 3664; 1907, **40**, 3903; *Annalen*, 1894, **281**, 312; 1896, **291**, 43; 1897, **297**, 3) depend on the use of the hydrochlorides of formimido-esters or of orthoformic esters. Used as additions to an alcoholic system in which acetalisation is taking place, these agents may be considered to affect the final yield of acetal by eliminating water irreversibly from the system in accordance with the equations

$$CH(OEt){:}NH,HCl + H_2O = NH_4Cl + H{\cdot}CO_2Et,$$
$$H{\cdot}C(OEt)_3 + H_2O = H{\cdot}CO_2Et + 2HOEt.$$

The agents used by Claisen are theoretically almost ideal ones for this purpose, but their cost militates very seriously against their general use for the economical preparation of acetals in large quantities, and searches for cheap substitutes have not been fruitful. Direct acetalisation, by acidified alcohol, of aldehydes which yield readily volatile acetals, which can be removed from the system by distillation, appears to be relatively simple in certain cases; but in the majority of instances, including those dealt with in the practical part of the present paper, the properties of the acetals probably do not admit of separation by fractional distillation. In Fischer's method, the aldehyde is dissolved in absolute alcohol containing about 1 per cent. of hydrogen chloride, and, when acetalisation is judged to be complete, the whole is poured into water containing sodium hydroxide or potassium carbonate to neutralise the mineral acid which serves as catalyst, and which, if allowed to remain, would tend to cause rapid hydrolysis of the acetal; the acetal is subsequently isolated with ether, for example, by extraction.

The foregoing procedure has several disadvantages. The very considerable excess of strong alcohol is recovered, if at all, in a highly dilute condition, and the mass of liquid to be extracted is very large. Moreover, workers who have attempted to follow it, especially, but not only, with large quantities of material, have frequently found it difficult to obtain the yields mentioned by Fischer, and this is possibly to be ascribed to the hydrolysis of acetal by the water used for dilution while the neutralisation is

locally incomplete. It is evident that both these drawbacks would be eliminated by neutralising the catalyst with an agent which during the operation did not increase the ratio, water : alcohol, in the system. For this purpose, ammonia or organic bases suggest themselves; but the authors' experiments indicate that ammonium chloride itself is an effective catalyst; for this reason, and because of the complications likely to ensue, the systematic experiments in this direction have not been pursued, although in some cases these compounds might be adapted for the purpose. Carbonates, etc., of the alkali metals, being insoluble in strong alcohol, introduce the danger of imperfect neutralisation of catalyst with fatal results on the yields; their use would also tend to increase the proportion of water in the system during neutralisation,

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$

and, from this point of view, alkaline hydroxides would be preferable, as, owing to their solubility in alcohol, they would be likely to effect neutralisation rapidly in the cold, a condition which is obviously necessary if the proportion of water increases while catalyst is present. Solutions of sodium ethoxide, or a mixture of hydroxide and ethoxide, in alcohol of such strength that the proportion of water in the system is not increased by the process of neutralisation, have advantages over all other agents, and such solutions may now be readily prepared without the use of metallic sodium, as experiments made in the laboratory by Mr. T. K. Walker have demonstrated. Slight excess of alkali seems to be of little consequence in most cases, and although the literature contains records of the manufacture of acetals with the aid of powerfully alkaline solutions (*Annalen*, 1857, **102**, 363; 1868, **146**, 193; *Jahresber.*, 1876, 336), it is probably not quite generally realised that most saturated acetals, whilst excessively sensitive to acids, are stable towards the strongest alkalis. Acetals thus resemble the "ortho-esters" of carboxylic acids, and, like these, have the properties of ethers. The hydrolytic effect of alkalis is apparently restricted to compounds containing the $>C{=}O$, $>C{=}N-$, and similar unsaturated groups. Whilst any serious effect of a very slight excess of alkali on the yield of acetal is seldom, if ever, to be feared, there is no doubt, with sensitive aliphatic compounds, a danger of some destruction of non-acetalised aldehyde during the recovery process. Experience with *iso*valeraldehyde, however, would indicate that, with reasonable care, loss due to this cause may be reduced to very small proportions.

Experimental.

In order to economise space, it may be stated at this point that each of the acetals prepared during the investigation was examined as to its behaviour towards acids, alkalis, and hydrogen sulphite solutions. In every case, dilute mineral acids caused rapid hydrolysis, but no appreciable effect was observed with cold, concentrated alkalis, even after very prolonged contact. Cold solutions of sodium hydrogen sulphite, if smelling of sulphur dioxide, appeared to attack the acetals, although usually somewhat slowly, but if the odour of sulphur dioxide was removed by cautious addition of bicarbonate, the solutions no longer had any appreciable effect on the acetals of the saturated acetals, but still reacted slowly with the acetals of cinnamaldehyde and citronellal, converting them in the course of some days into pasty or even semi-solid masses. It seems not improbable that in these cases addition may take place at the αβ-unsaturated linking even in absence of the free aldehyde group; the speed of the change, however, is not so great as to render the use of such "neutralised bisulphite" impracticable for the purpose of removing free aldehyde from the crude acetal.

The ethyl alcohol used in all the experiments was dried by Winckler's method, with all precautions to ensure presence of dissolved calcium ethoxide in the alcohol before distillation. The "alcoholic hydrogen chloride" was made by passing into such alcohol 1 per cent. of dry hydrogen chloride, and the "alcoholic sodium ethoxide" by dissolving in it metallic sodium. In all instances, unless a statement to the contrary occurs, the acetals were isolated as follows: To the solution in which acetalisation had been carried out, there was added enough alcoholic sodium ethoxide to neutralise the mineral acid present, phenolphthalein being used as indicator. The alcohol was removed by distillation in a vacuum, the distilling flask being immersed during this process in a bath heated at about 30°. The residue left in the flask was then shaken with excess of a solution of sodium hydrogen sulphite to which enough sodium hydrogen carbonate had been added to remove all odour of sulphur dioxide ("neutralised bisulphite solution") and the undissolved oil extracted with ether. Finally, the ethereal extract was dried over solid potassium carbonate, evaporated, and the acetal purified by fractionation in a vacuum.

The percentage yields given represent in all cases the yield as compared with that theoretically possible. "Corrected" yields are calculated in the same way, but include the quantities of acetal volatilised in removing the excess of alcohol under the foregoing

condition, quantities which in a number of cases had to be determined by finding the loss experienced in working up known quantities in the same manner. The majority of the initial experiments were carried out in connexion with the conversion of benzaldehyde into its diethylacetal. This acetal is distinctly volatile in vapour of alcohol. It was found, for example, that under the conditions actually used for recovery of alcohol after acetalisation, about 1·4 grams of acetal out of a total of 11·4 grams were carried over with 100 c.c. of alcohol, and from a series of such observations a means of correcting the yields was secured. The acetal lost by proceeding in the foregoing manner could no doubt be retained by using an efficient column when operating on a large scale.

Conversion of Benzaldehyde into its Diethylacetal.

Process A.—A series of experiments was carried out on the acetalisation of benzaldehyde with 1 per cent. alcoholic hydrogen chloride (p. 79) at about 18°, the acetal formed being estimated as above described. It was found that after two days no further increase in the yield could be detected. The following results were obtained by varying the ratio of alcohol to benzaldehyde :

	A.	*B.*	*C.*	*D.*	*E.*
Ratio of alcohol : benzaldehyde by weight	4·04	8·06	10·2	16·3	31·5
Percentage of acetal actually isolated	52·3	55·5	56·5	56·5	54·5
Correction for loss by volatilisation	3·1	6·6	8·5	13·1	25·8
Total percentage yield	55·5	62·1	65·0	69·6	80·3

It may be noted that the yield actually obtained by operating in the above way was decidedly larger than that obtained by Fischer when using the same proportions of alcohol and benzaldehyde.

Study of the table given indicates clearly that whilst the total quantity of acetal formed may be greatly increased by raising the proportion of alcohol, there is in practice a proportion which it would not be economical to exceed, having regard to cost of recovery of material used. Under laboratory conditions, this proportion is perhaps about 5 to 8, according to the efficiency of the column used in removing excess of alcohol.

Attempts were made to ascertain whether the ideal dehydrating agents used by Claisen, namely, ethyl orthoformate and ethyl imidoformate, could be replaced by ethyl orthoborate, or by silicon tetrachloride, but the yield was not improved by addition of the former of these, and was depressed by the latter.

Process B. An Adaptation of Young's Method of Dehydration of Alcohol to the Preparation of Acetals.—One part by weight of benz-

aldehyde was dissolved in 10 parts by weight of alcoholic hydrogen chloride and 17 parts by weight of benzene, and the whole heated to boiling in an apparatus of glass constructed so that the vapours containing the ternary mixtures of alcohol, benzene, and water were condensed and returned automatically to a flask containing excess of calcium carbide; this flask was heated in an oil-bath at 110—120° and the partly dried vapours from it were liquefied in a second condenser and returned to the original vessel, in which acetalisation was taking place. After thirty hours, the heating of the first vessel was discontinued, tbe whole of the liquid from the flask of carbide allowed to volatilise into it, and then the liquid was cooled and worked up as in the previous experiments. The weight of acetal actually isolated was 66 per cent. of the quantity theoretically possible, and this compares very favourably with the figure (36 per cent.) obtained by Fischer's original method. If correction be made for the amount of acetal volatilised in the recovery of alcohol, the total yield works out to 74 per cent.

Use of Ammonium Chloride as Catalyst.

Claisen (*Ber.*, 1907, **40**, 3906) used this salt as catalyst in effecting acetalisation of aldehydes and ketones by means of ethyl orthoformate, but the applieation of this agent in place of hydrogen chloride in direct acetalisation by alcohol does not seem to have been tried.

The present authors have found that benzaldehyde, when left with anhydrous alcohol containing 0·6 per cent. of its weight of ammonium chloride for two days and worked up by the sodium ethoxide method, gives a yield of acetal only about 5 per cent. less than when hydrogen chloride is used as catalyst. When applied by method *B*, the results are even better than with hydrogen chloride, and in an experiment closely corresponding with the one above described in detail a yield of acetal amounting to 74 per cent. was realised, or 82·4 per cent. when corrected for loss due to volatility in alcohol vapour.

Anisaldehyde.

The diethylacetal of the aldehyde closely resembles that of benzaldehyde, but is less volatile in alcohol vapour. The authors obtained it in yield rather less than 40 per cent. by the application of cold alcoholic hydrogen chloride for four days, or by boiling with alcohol containing ammonium chloride (0·6 per cent.), the product being worked up in both instances by the sodium ethoxide

method. Fischer's method has been applied to the preparation of the dimethylacetal only.

Piperonal.

Piperonal is decidedly more difficult to convert into acetal than is either benzaldehyde or anisaldehyde. Fischer obtained a yield of dimethylacetal amounting to only 25 per cent. Using hydrogen chloride as catalyst in the cold or ammonium chloride at the boiling point of alcohol, the present authors were able to isolate *22 per cent. and 25 per cent. respectively* of diethylacetal. It is probable, therefore, that these quantities correspond fairly closely with quantities present at equilibrium when the initial ratio of piperonal to alcohol is about 1 : 10.

Cinnamaldehyde.

This was selected as an example of an unsaturated fatty-aromatic aldehyde. Its dimethylacetal has been obtained both by Fischer and by Claisen. Applying much the same conditions for preparing this acetal as were used by Fischer in making the corresponding dimethylacetal (*Ber.*, 1898, **31**, 1990), but working up the product by the sodium ethoxide method and removing unchanged aldehyde by rapid treatment with "neutralised bisulphite solution," a 35 per cent. yield of acetal was obtained; this figure, corrected for loss due to volatility in alcohol, corresponds with a total of 40 per cent. of the theoretical quantity. There is considerable formation of brown tar, no matter how the product is worked up. By reducing the proportion of hydrogen chloride to 0·7 per cent. and prolonging the action for four days, the yield was increased by 3—4 per cent. Using ammonium chloride (0·6 per cent.) as catalyst, the total quantity of acetal formed after five days in the cold was 42 per cent., *but in this instance there was no formation of tar*, and nearly the whole of the non-acetalised aldehyde was recovered as oxime.

It does not appear to be advantageous in the case of cinnamaldehyde to apply the modified Young dehydration process (p. 80), as, owing to the heating necessary, much tar is formed even when ammonium chloride is used, and there is loss both of aldehyde and acetal.

Citronellal and Citral.

The dimethylacetal of citronellal has been prepared by Harries (*Ber.*, 1900, **33**, 857), who used Fischer's *method and obtained it in 56 per cent. yield.* The present authors isolated the diethylacetal

(b. p. 122—125°/12 mm.) in 60 per cent. yield by leaving citronellal with five times its volume of alcoholic hydrogen chloride at the ordinary temperature for eight days, then working the product by the hydrogen sulphite method and using a column in recovering excess of alcohol. A yield of about 50 per cent. was obtained when the aldehyde was boiled with ten times its volume of alcohol containing ammonium chloride (0·6 per cent.) as catalyst.

There is but little formation of tarry products when citronellal is acetalised in either of the above ways, and the bulk of the aldehyde which has escaped acetalisation can be recovered. In these respects, the aldehyde differs greatly from citral, which yields not more than 15 per cent. of product having the properties of an acetal (b. p. 140—142°/15 mm.) and is mainly converted into tarry products.

iso*Valeraldehyde.*

The diethylacetal of *iso*valeraldehyde has previously been made by Alsberg (*Jahresber.*, 1864, 485), who describes it as an oil having a pleasant, fruity odour and boiling at 158·2°. In the experiments made by the present authors, the acetal isolated boiled at 152—153°.

Although appreciably volatile with alcohol vapour, especially during recovery from alcoholic solution with the aid of a vacuum, the acetal may be separated from alcohol with little loss by distilling at the ordinary pressure and using a column.

Using Fischer's method for acetalisation, but working up the product after nine days in the cold by the sodium ethoxide method, the acetal was isolated in yield amounting to 32 per cent. of that theoretically possible, whilst nearly the whole of the remainder of the aldehyde was recovered as sodium hydrogen sulphite compound. Using ammonium chloride (6·6 per cent.) as catalyst and boiling for twelve hours, the same yield of acetal as before was obtained, and a slight improvement was effected by applying the modified Young dehydration process (p. 80). Most of the aldehyde which escaped acetalisation was found as bisulphite compound in the wash-liquors.

m-*Nitrobenzaldehyde.*

Fischer has previously prepared the dimethylacetals of *o*- and *p*-nitrobenzaldehydes by his process, the yields being 70 and 77 per cent. respectively. The present authors, by leaving *m*-nitrobenzaldehyde for six days with five times its weight of alcoholic hydrogen chloride and working up the product by the sodium ethoxide process, obtained a yield of diethylacetal corresponding

with 78 per cent. of the theoretical amount. The acetal had the properties assigned it by Claisen (*Ber.*, 1898, **31**, 1016).

Reduction of m-*Nitrobenzaldehydediethylacetal.*

The reduction of nitro-acetals in the aromatic series does not seem to have been previously accomplished. The authors effected the reduction of *m*-nitrobenzaldehydediethylacetal as follows: Sodium sulphide crystals (50 grams) were dissolved in water (50 c.c.) and partly converted into the hydrosulphide by addition of concentrated hydrochloric acid (25 grams); the resulting solution, which had an alkaline reaction, was added to alcohol (90 c.c.) containing 15 grams of the acetal, when heat was evolved and the mixture became red. Reduction was completed by boiling for six hours, the alcohol was then removed by distillation through a column, and the residue, which still showed a distinct alkaline reaction, was cooled and extracted with ether. Evaporation of the washed and dried ethereal extract yielded a yellow oil, which was freed from volatile impurities by heating for some time in a vacuum at 100°. There is little doubt that the above oil was impure m-*aminobenzaldehydediethylacetal*. It contained no free aldehyde, as it was unaffected by cold "neutralised bisulphite" solution, free hydroxylamine, or phenylhydrazine. It was nearly insoluble in water, but dissolved in dilute mineral acid, being at once converted into a salt of *m*-aminobenzaldehyde, which was precipitated in a powder on subsequent addition of alkali. Heated with hydriodic acid, the oil gave off a volatile liquid, evidently ethyl iodide, and with a mixture of benzoic and sulphuric acids evolved the odour of ethyl benzoate. The behaviour of the oil towards phenylcarbimide is somewhat striking; considerable evolution of heat occurs on mixing, and a yellow precipitate separates; this, when purified, melts at 168°, and appears to consist exclusively of the phenylcarbamide derived from the aminoaldehyde (Found: C = 70·3; H = 5·1; N = 11·9. $CHO \cdot C_6H_4 \cdot NH \cdot CO \cdot NH \cdot C_6H_5$ requires C = 70·0; H = 5·0; N = 11·7 per cent.), as it gives no test for acetal, but reacts at once with phenylhydrazine, giving a phenylhydrazone which forms yellow crystals melting at 196° (Found: C = 72·9; H = 5·7; N = 17·1. $C_{20}H_{18}ON_4$ requires C = 72·7; H = 5·5; N = 17·0 per cent.). In similar manner, when the aminoacetal is shaken with benzoyl chloride suspended in aqueous sodium hydroxide solution, even when the conditions are maintained alkaline throughout, the odour of ethyl benzoate becomes perceptible and the crystalline product obtained (m. p. 115—116°) is the benzoyl derivative of *m*-aminobenzaldehyde

(Found: C = 74·4; H = 4·9; N = 6·3. $CHO·C_6H_4·NH·CO·C_6H_5$ requires C = 74·7; H = 5·0; N = 6·2 per cent.), as indicated by response to tests for free aldehyde (phenylhydrazone, m. p. 212°. Found: C = 75·8; H = 5·5; N = 13·5. $C_{20}H_{17}ON_3$ requires C = 76·2; H = 5·4; N = 13·3 per cent.) and by the negative results obtained on applying tests for the acetal complex.

The aminoacetal in ethyl acetate solution yields a crystalline precipitate with picric acid, but this is a picrate of the free aldehyde.

Thus, whilst the aminoacetal does not respond to any test distinctive of free aldehyde, it reacts with agents which attack the free amino-group, but in all the cases examined only the derivatives of the aldehyde and not of the acetal have been isolated and it has not yet been determined whether this result may be modified by rigid exclusion of moisture.

Summary.

The complete stability of acetals towards alkalis and their great sensitiveness to acids render it possible to foresee the conditions necessary to avoid reversal of the acetalisation of aldehydes by alcoholic hydrogen chloride, and one process is described which satisfies these conditions and permits of the ready isolation of numerous acetals and recovery of excess of strong alcohol.

Ammonium chloride may be used as catalyst in place of the hydrogen chloride in Fischer's process for acetalisation. By adapting Young's process for the dehydration of alcohol by distillation with benzene, and using ammonium chloride as catalyst, larger yields of acetal than by Fischer's original method may be obtained.

Cold aqueous solutions of sodium hydrogen sulphite, which have been freed from all odour of sulphur dioxide by means of sodium hydrogen carbonate, have no action on the acetals of the saturated aldehydes which have been examined, but very slowly alter the acetals of cinnamaldehyde and of citronellal.

m-Nitrobenzaldehydediethylacetal may be reduced to *m*-aminobenzaldehydediethylacetal by means of an alkaline solution of sodium hydrosulphide.

It is desired to acknowledge a grant made to one of us (R. D. H.) by the Department of Scientific and Industrial Research, with the aid of which some of the work described was carried out.

ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER. [*Received, December 1st, 1921.*]

XV.—*The Interaction of Aromatic Disulphides and Sulphuric Acid.*

By SAMUEL SMILES and ERNEST WILSON McCLELLAND.

FROM the behaviour of aromatic disulphides in presence of sulphuric acid, evidence has been adduced to show that the equilibrium represented by the following expression is established:

$$R\cdot S\cdot S\cdot R + H_2O \rightleftharpoons R\cdot S\cdot OH + HS\cdot R.$$

In all the cases examined this hydrolysis appears to take place only in solution in the concentrated acid, and when water is added the greater part of the insoluble disulphide is recovered. If this hypothesis be a correct interpretation of the state of a disulphide in such solution, it follows that the addition of another disulphide or mercaptan should result in the formation of an unsymmetrical disulphide in the equilibrium mixture:

$$R\cdot S\cdot OH + HS\cdot R' \rightleftharpoons H_2O + R\cdot S\cdot S\cdot R'$$

or

$$R\cdot SH + HO\cdot S\cdot R' \rightleftharpoons H_2O + R\cdot S\cdot S\cdot R'.$$

The experiments now described were carried out with the object of submitting the hypothesis to this further test. The experimental difficulties involved are considerable, for a reacting mixture such as that described would contain three disulphides and the isolation of the unsymmetrical compound would in most cases be uncertain. This circumstance has been met in the following manner. By taking one disulphide in large excess the product should consist chiefly of two disulphides: the unsymmetrical compound and that taken in excess; the separation of these two and the third disulphide present only in small amount was rendered more easy by choosing reacting disulphides of widely different physical properties. The materials employed in one series of experiments were 2 : 2′-dithiobenzoic acid and dithioglycollic acid; the unsymmetrical disulphide, 2-carboxyphenyldithioglycollic acid, $HO_2C\cdot C_6H_4\cdot S\cdot S\cdot CH_2\cdot CO_2H$, was isolated from the solution of these substances in sulphuric acid. The prolonged action of hot sulphuric acid with this substance leads to an interesting result; a product is formed which contains the dithiobenzoyl group, and the fact gives important evidence of the presence of the dithio-arrangement in the substance.

Since the condensation of the 2-thiobenzoic and thioglycollic groups may be thus effected, the investigation was extended to the interaction of hydrogen sulphide with 2-thiolbenzoic acid or the corresponding disulphide. With these reagents it is to be expected,

in accordance with the hypothesis described, that an unsymmetrical disulphide containing the structure of a thiosulphenic acid should be formed :

$$R\cdot S\cdot OH + H\cdot SH \rightleftharpoons R\cdot S\cdot SH + H_2O.$$

Very little is known of this class of compound, in fact the β-naphthyl derivative, which was obtained by White (T., 1918, **113**, 608) from the interaction of sodium disulphide and β-naphthyl disulphide, appears to be the only representative hitherto isolated. In presence of sulphuric acid, which has been employed in the experiments now described, there is little doubt that a thiosulphenic acid would not survive, but, like all compounds containing the sulphydryl group, would be oxidised, yielding the tetrasulphide or a polysulphide and sulphur :

$$2R\cdot S\cdot SH + O = R\cdot S\cdot S_2\cdot SR + H_2O.$$

By the use of 2-thiolbenzoic acid, this result is avoided and a simple product, 2-dithiobenzoyl (I), is formed by intramolecular condensation ;

$$C_6H_4{<}{}^{S\cdot SH}_{CO\cdot OH} \qquad\qquad C_6H_4{<}{}^{S-}_{CO}{>}S$$

(II.) (I.)

The compound, being volatilised by steam, is readily isolated. This substance is very easily obtained from other sources. For example, the 2-polythiobenzoic acid obtained at an intermediate stage of the preparation of 2-thiolbenzoic acid (D.R.-P. 205450) yielded 2-dithiobenzoyl when warmed with sulphuric acid. It is evident that in this reaction the polysulphide chain is broken and that among the fragments the dithiobenzoyl group occurs probably as 2-thiosulphenylbenzoic acid (II). Warm sulphuric acid decomposes the unsymmetrical disulphide mentioned in a foregoing paragraph, the formation of 2-dithiobenzoyl being effected by rupture of the thioglycollyl group.

$$C_6H_4{<}{}^{S\cdot S\cdot CH_2\cdot CO\cdot OH}_{CO\cdot OH} \longrightarrow C_6H_4{<}{}^{-S}_{CO}{>}S \qquad C_6H_4{<}{}^{CO}_{CO}{>}S$$

(III.)

Finally, it may be mentioned that phthalyl sulphide (III) and 2-thiolbenzoic acid yield this compound under the same conditions.

With the possible exception of dehydrodithionmalonanilide (Reissert and Moré, *Ber.*, 1906, **39**, 3302), the heterocyclic system contained by 2-dithiobenzoyl does not appear to have been previously encountered. It is remarkably resistant to the action of acids; the substance may be boiled with dilute mineral acids, and may even

be heated at 90° with concentrated sulphuric acid, without undergoing change. Moreover, contrary to anticipation, it does not yield thioxanthone under the same conditions as 2-thiolbenzoic acid. The substance is not so stable in presence of alkaline reagents; and although it is not attacked by cold aqueous sodium hydroxide and only slowly by the hot medium, it readily yields to the influence of sodium ethoxide, 2-dithiobenzoic acid being formed. Boiling aniline reacts in a similar manner, yielding the anilide of 2-dithiobenzoic acid (IV). Aqueous sodium sulphide quickly dissolves

$$\left[C_6H_4{<}{\genfrac{}{}{0pt}{}{\text{—S—}}{CO\cdot NHPh}}\right]_2 \qquad C_6H_4{<}{\genfrac{}{}{0pt}{}{S\cdot SH}{CO\cdot SH}} \qquad ClMe_2N : C_6H_3{\lessgtr}{\genfrac{}{}{0pt}{}{S}{N}}{>}S$$

(IV.) (V.) (VI.)

2-dithiobenzoyl, giving yellow solutions containing the sodium salt of an unstable acid, probably the trithio-compound (V); but when the latter is set free by mineral acid the cyclic compound is regenerated. *In view of the stability and various modes of formation of* this cyclic system it is interesting to notice that the analogous dithio-*imino*-group *is capable of existence.* In this case also, only one representative (compare Eng. Pat. 17417) appears to be known; this has been termed methylene-red (VI), and was obtained by Bernthsen (*Annalen*, 1885, **230**, 137; 1889, **251**, 19) from the oxidation of 5-dimethylamino-2-aminophenyl mercaptan in presence of excess of hydrogen sulphide. The process of formation is thus similar to those of 2-dithiobenzoyl, and the stability is of the same character, for the substance resists boiling dilute acids, but is resolved by alkaline reagents into 5 : 5′-tetramethyldiamino-2 : 2′-*diaminodiphenyl* disulphide.

Experimental.

2-Carboxyphenyldithioglycollic Acid, $HO_2C\cdot C_6H_4\cdot S_2\cdot CH_2\cdot CO_2H$.

A solution of 3 grams of thiolglycollic acid in 10 c.c. of concentrated sulphuric acid *was kept at 45° for half an hour or until* conversion to the disulphide was complete. One gram of 2-thiolbenzoic acid or the corresponding disulphide suspended in 10 c.c. of sulphuric acid was added, the mixture being then constantly shaken and kept at 30°. After the lapse of about fifteen minutes the solution was poured over crushed ice, then the solid which separated was collected and treated with boiling water. A small quantity of the insoluble 2-dithiobenzoic acid was removed and the solution set aside to cool, when the required disulphide separated in the crystalline state. The product was purified by fractional precipitation with water from the alcoholic solution, 2-carboxy-

phenyldithioglycollic acid being thus obtained in small, colourless needles which melted at 181—183° (Found: C = 44·5; H = 3·5. $C_9H_8O_4S_2$ requires C = 44·2; H = 3·3 per cent.). The substance is sparingly soluble in cold water, but readily so in the hot medium and in most organic solvents. The solution in sulphuric acid exhibits a green fluorescence; in the warm medium the substance is decomposed. The instability of the disulphide is clearly shown by the prolonged action of boiling water, which produces among other substances 2-dithiobenzoic acid. The formation of this product may be interpreted by the hydrolysis of the unsymmetrical disulphide,

$$H_2O + Ar{\cdot}S{\cdot}S{\cdot}R \rightleftharpoons Ar{\cdot}S{\cdot}OH + R{\cdot}SH$$
$$H_2O + Ar{\cdot}S{\cdot}S{\cdot}R \rightleftharpoons Ar{\cdot}SH + R{\cdot}S{\cdot}OH$$

and the formation of the most stable and least soluble disulphide from the fragments:

$$Ar{\cdot}S{\cdot}OH + HS{\cdot}Ar \rightleftharpoons H_2O + Ar{\cdot}S{\cdot}S{\cdot}Ar.$$

The assumption that hydrolysis of this disulphide may be thus effected by boiling water is supported by the fact that some symmetrical aromatic disulphides are decomposed by a cold dilute solution of sodium hydroxide (T., 1921, **119**, 1792).

2-Dithiobenzoyl (Formula I).

(*a*) *From 2-Thiolbenzoic Acid and Hydrogen Sulphide.*—A current of hydrogen sulphide was passed at intervals through a solution of 5 grams of 2-thiolbenzoic acid in 50 c.c. of sulphuric acid at 45°. After each addition of hydrogen sulphide the mixture was thoroughly shaken. Finally, the cold reacting mixture was poured over ice, and the resulting liquid was treated with a current of steam. The volatile solid contained uncombined sulphur, which was removed by renewed treatment with steam in presence of powdered iron. The product was again collected and recrystallised from aqueous alcohol. The same substance was obtained by heating 2-polythiobenzoic acid with sulphuric acid and submitting the product to a similar process of purification.

(*b*) *From 2-Thiolbenzoic Acid and Thiolglycollic Acid.*—A mixture of 5 grams of 2-thiolbenzoic acid and an equal weight of dithioglycollic acid was heated with 100 c.c. of sulphuric acid for two hours at 50—60°. The resulting solution was treated with ice-cold water and the product purified by volatilisation with a current of steam. Similar treatment of 2-carboxyphenyldithioglycollic acid in presence of dithioglycollic acid yielded the same product.

(*c*) *From 2-Thiolbenzoic Acid and Phthalyl Sulphide.*—A solution of 1 gram of the acid and 1·2 grams of phthalyl sulphide in 20 c.c. of sulphuric acid was heated for two hours at 50°. The product, which was obtained as in the foregoing preparation, contained a small amount of phthalyl sulphide; this impurity was removed by shaking the ethereal solution with cold dilute aqueous sodium hydroxide.

The products of these several methods of preparation were identical. 2-Dithiobenzoyl crystallises from aqueous alcohol in slender, pale yellow needles; it melts at 77° and is readily soluble in most organic media (Found: C = 49·9; H = 2·7; S = 38·2; *M* = 161. $C_7H_4O_2S_2$ requires O = 49·94; H = 2·39; S = 38·13 per cent.; *M* = 168). Although unattacked by dilute aqueous alkali hydroxide, the substance is readily decomposed by a warm solution of sodium ethoxide, 2-dithiobenzoic acid being formed. Aqueous sodium sulphide dissolves 2-dithiobenzoyl, giving a yellow solution from which the cyclic compound is recovered by the addition of a mineral acid. Reduction with zinc dust in warm acetic acid yields hydrogen sulphide, zinc sulphide, and the colourless form of 2-thiolbenzoic acid, which melts at 164—165° (Hinsberg, *Ber.*, 1910, **43**, 652). With an ammoniacal solution of silver oxide the substance rapidly yields silver sulphide.

Reaction of Aniline with 2-Dithiobenzoyl.—A solution of the thio-compound in aniline was boiled for three hours, then cooled and treated with excess of dilute hydrochloric acid. The solid product was collected and treated successively with water and with a little hot alcohol. The residue was crystallised from hot glacial acetic acid, when the pure product was obtained in small, colourless needles which melted at 239—240°. The nature of this substance was proved by comparison with the dianilide of 2-dithiobenzoic acid, which was prepared by the action of hot aniline with the dichloride of 2-dithiobenzoic acid (*Ber.*, 1898, **31**, 1670). The product obtained by this process was purified by the usual methods and was found to be identical with that isolated from the interaction of aniline and 2-dithiobenzoyl. It melted at the same temperature as the latter, whether heated alone or mixed with it (Found: N = 6·6. $C_{26}H_{20}O_2N_2S_2$ requires N = 6·14 per cent.).

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XVI.—*Organo-derivatives of Bismuth. Part V. The Stability of Halogen, Cyano-, and Thiocyano-derivatives of Tertiary Aromatic Bismuthines.*

By FREDERICK CHALLENGER and JOHN FREDERICK WILKINSON.

THE dihaloids of triphenylbismuthine show diminished stability with increase in the positive character of the halogen until, with iodine, the di-iodide, Ph_3BiI_2, has not been isolated but immediately decomposes, giving iodobenzene and diphenyliodobismuthine (Challenger and Allpress, T., 1915, **107**, 21; Gillmeister, *Ber.*, 1897, **30**, 2843). As a result of work described in this and in previous communications, the relations existing between the dihaloids and similar derivatives may be summarised thus—

	M. p.	Temp. of Decomposition.
Difluoride	159°	190—200°
Dichloride	141°	150°, and slowly in boiling benzene.
Dibromide	122°	100°, and easily in boiling benzene.

Di-iodide, not isolated, unstable, yielding Ph_2BiI and PhI.
Dicyanide, not isolated, unstable, yielding $Ph_2Bi{\cdot}CN$ and $Ph{\cdot}CN$.
Dithiocyanate, not isolated, unstable, yielding $Ph_2Bi{\cdot}SCN$ and $Ph{\cdot}SCN$.

The decomposition of the dihaloids may be represented by the equations—

$$\text{(i)}\ Ph_3BiX_2 = Ph_2BiX + PhX$$

$$\text{or} \quad \text{(ii)}\ 2Ph_3BiX_2 = Ph_3Bi + PhBiX_2 + 2PhX$$

and at a higher temperature,

$$\text{(iii)}\ 2Ph_3Bi = 3Ph_2 + 2Bi.$$

When triphenylbismuthine dichloride is treated with potassium fluoride in aqueous-alcoholic solution, ***triphenylbismuthine difluoride***, m. p. 159°, is produced. This decomposes when heated, giving fluorobenzene, triphenylbismuthine, diphenyl, and probably bismuth fluoride. Although no tetraphenylbismuthonium haloids have so far been obtained, the stability of the difluoride led us to hope that, by interaction with magnesium phenyl bromide, tetraphenylbismuthonium fluoride might possibly be formed, but only triphenylbismuthine was isolated.

The action of potassium hydrogen fluoride on triphenylbismuthine dichloride differs from that of the normal fluoride, triphenylbismuthine being obtained. The production of this substance from potassium fluoride and diphenylbromobismuthine (p. 101) appears to

be analogous, and is possibly due to the production of potassium hydroxide by hydrolysis (see p. 94; and Challenger and Goddard, T., *1920*, **117**, *766*).

The course of the reaction between diphenylbromobismuthine and silver nitrate depends on the temperature and possibly on the time of interaction. In boiling alcohol, silver bromide, bismuth oxynitrate, and sometimes triphenylbismutbine are produced, whilst reaction in the cold yields the bismuthine, bismuth salts, diphenyl, silver bromide, and metallic silver. Probably the first product is *diphenylbismuthine nitrate*, Ph_2BiNO_3, which may react with water, forming benzene and bismuth oxynitrate. It may also be hydrolysed to nitric acid and diphenylhydroxybismuthine, $Ph_2Bi{\cdot}OH$, which would then yield triphenylbismuthine and bismuth hydroxide (Michaelis and Marquardt, *Annalen*, 1889, **251**, 323). Challenger and Allpress (T., *1921*, **119**, *916*) have shown that triphenylbismuthine and silver nitrate give a yellow, crystalline precipitate, probably having the composition $AgNO_3,2AgPh$, a compound which has been described by Krause and Schmidt (*Ber.*, 1919, **52**, 2150). This compound would probably decompose, giving metallic silver and diphenyl *—

$$AgNO_3,2AgPh = AgNO_3 + 2Ag + Ph_2.$$

This would be analogous to the behaviour of alkyl and aryl plumbanes, which also reduce silver nitrate to the metal, giving organo-silver compounds as intermediate products (Krause and Schmidt, *loc. cit.*).

From lead thiocyanate and diphenylbromobismuthine in alcoholic solution, triphenylbismuthine and *diphenylthiocyanobismuthine*, $Ph_2Bi{\cdot}SCN$, were obtained. The production of triphenylbismuthine is due to decomposition of the diphenylthiocyanobismuthine in alcoholic solution, a reaction which has been observed during the purification of this substance, and which is analogous to the behaviour of diphenylcyanobismuthine (T., 1915, **107**, 20)—

$$3Pb_2Bi{\cdot}SCN = 2Ph_3Bi + Bi(SCN)_3.$$

Diphenylcyanobismuthine was also obtained from diphenylbromobismuthine and potassium cyanide in aqueous-alcoholic solution.

In an attempt to obtain the unknown dicyanide, $Ph_3Bi(CN)_2$, from the dichloride and alcoholic potassium cyanide, diphenyl-

* Mr. A. L. Smith has shown that diphenylbromobismuthine and silver fluoride in the cold give silver bromide, bismuth fluoride, diphenyl, and metallic silver.

cyanobismuthine was isolated, which may be explained by the elimination of benzonitrile from the dicyanide. When the dry dichloride and silver cyanide are gently heated, the odour of benzonitrile is apparent at 75°. It was hoped that the unknown triphenylbismuthine *dithiocyanate*, $Ph_3Bi(SCN)_2$, *might be obtained by* treating the dichloride with silver thiocyanate in cold alcohol, but no reaction occurred.

When lead thiocyanate and triphenylbismuthine dichloride were heated to about 85°, phenyl thiocyanate was produced.

From lead thiocyanate and an alcoholic solution of triphenylbismuthine dichloride, diphenylthiocyanobismuthine, phenyl thiocyanate, and polymerised thiocyanogen, $(SCN)_x$ (Söderbäck, *Annalen*, 1919, **419**, 217) were isolated.

An attempt to obtain triphenylbismuthine dithiocyanate by the addition of free thiocyanogen, $(SCN)_2$, prepared according to the method of Söderbäck (*loc. cit.*), to triphenylbismuthine in ethereal solution was also unsuccessful, the products being bismuth thiocyanate (Bender, *Ber.*, 1887, **20**, 723), phenyl thiocyanate, and diphenylthiocyanobismuthine, which has therefore been prepared by three different methods. This is analogous to the action of thiocyanogen on mercury diphenyl, giving mercury phenyl thiocyanate and phenyl thiocyanate (Söderbäck, *loc. cit.*). The production of the small quantity of bismuth thiocyanate might be caused by further substitution, or decomposition of the diphenylthiocyanobismuthine as above.

From these results, it is obvious that triphenylbismuthine dicyanide and dithiocyanate—as well as the di-iodide—are extremely unstable compounds, a property which is shared by the corresponding salts of copper.

This being the case, it was of interest to determine whether the cyano- or the thiocyano-radicle possesses the greater affinity for bismuth. For this purpose, cyanogen sulphide, $(CN)_2S$ (Schneider, *J. pr. Chem.*, 1885, [ii], **32**, 187), and triphenylbismuthine were shaken with dry ether for eleven hours, yielding bismuth thiocyanate, unchanged triphenylbismuthine, diphenylthiocyanobismuthine, and phenyl thiocyanate. No diphenylcyanobismuthine was isolated. Other experiments confirmed these results, and the reaction is being further investigated.

A similar lack of success attended our efforts to prepare the dicyanide and dithiocyanate of tri-α-naphthylbismuthine. Lead thiocyanate and tri-α-naphthylbismuthine dichloride in boiling alcohol gave *α-naphthyl thiocyanate*, and tri-α-naphthylbismuthine. No α-naphthylthiocyanobismuthines were detected, due probably to their instability.

The hypothetical dithiocyanate probably breaks down thus :—

$$(C_{10}H_7)_3Bi(SCN)_2 = (C_{10}H_7)_2Bi{\cdot}SCN + C_{10}H_7{\cdot}SCN.$$
$$3(C_{10}H_7)_2Bi{\cdot}SCN = 2(C_{10}H_7)_3Bi + Bi(SCN)_3.$$

α-Naphthyl thiocyanate does not appear to have been described.* It was also obtained from tri-α-naphthylbismuthine and thiocyanogen, together with bismuth thiocyanate, thus :—

$$(C_{10}H_7)_3Bi + 3(SCN)_2 = 3C_{10}H_7{\cdot}SCN + Bi(SCN)_3.$$

With potassium cyanide in boiling alcohol, tri-α-naphthylbismuthine dichloride gave the bismuthine. This may be due to the action of alkali, arising from the hydrolysis of potassium cyanide, on di-α-naphthylcyanobismuthine (compare p. 92; and Challenger and Allpress, T., 1921, **119**, 914).

Triphenylbismuthine dichloride was prepared by Michaelis and Marquardt (*loc. cit.*) by the action of chlorine on the bismuthine in chloroform, but no mention is made of the simultaneous production of a small quantity of diphenylchlorobismuthine, which may be isolated on crystallisation from acetone, in which it is sparingly soluble. This probably explains the low m. p. of the dichloride, when recrystallised from chloroform–light petroleum. The m. p. of the pure dichloride has, however, been shown to depend on the rate of heating, being somewhat higher when rapidly heated, and in the case of large crystals.

Potassium cyanate and triphenylbismuthine dichloride, when heated with alcohol, regenerated the free bismuthine, this being probably due to hydrolysis of the potassium cyanate. No reaction occurred in the cold.

Kipping and Sands (T., 1921, **119**, 842) have shown that with *s*-tetrachloroethane, certain silico-hydrocarbons give dichloro-additive products. Its action on tertiary bismuthines has been investigated, triphenylbismuthine yielding diphenylchlorobismuthine. No dichloride was isolated, even on heating for only a few seconds, although this compound is probably formed in the first instance. No reaction occurred in the case of tri-α-naphthylbismuthine, even on boiling for several hours.

Michaelis and Marquardt (*loc. cit.*) state that chloroform and triphenylbismuthine in a sealed tube at 150° give a charred mass and hydrogen chloride, the production of triphenylmethane being assumed. At 150—160°, contrary to the statement of these authors,

* Gattermann and Hausknecht (*Ber.*, 1890, **23**, 738) state that it is obtained by way of the diazo-reaction and cuprous thiocyanate, but give no details. We have prepared α-naphthyl thiocyanate by this method, but in very poor yield, and find it to be identical with the product obtained from tri-α-naphthylbismuthine dichloride.

the mixture did not char, but consisted of hydrogen chloride, bismuth chloride, and triphenylmethane in very small quantity. This would appear analogous to the action of chloroform on magnesium diphenyl (Waga, *Annalen*, 1894, **282**, 320). On attempting to increase the amount of triphenylmethane by heating at 130—140° for ten hours, none was detected, but an odour of ethyl benzoate was observed, and diphenylchlorobismuthine produced. The reaction probably proceeds in stages, the first being—

$$Ph_3Bi + CHCl_3 = Ph_2BiCl + PhCHCl_2.$$

The production of ethyl benzoate was probably due to the action of air and impurities in the chloroform on benzal chloride.

Magnesium benzyl chloride (6 mols.) and diphenylbromobismuthine yielded triphenylbismuthine and inorganic compounds of bismuth. Neither diphenylbenzylbismuthine nor tribenzylbismuthine was isolated, and this is in agreement with the failure to obtain arylalkylbismuthines, such as diphenylethylbismuthine and diphenyl*iso*butylbismuthine (Challenger, T., 1914, **105**, 2216; 1916, **109**, 250).

The absence of tribenzylbismuthine is not surprising, since it is readily oxidised to benzaldehyde in the presence of air and moisture (Challenger and Ridgway, this vol., p. 112).

Diphenyl-α-naphthylbismuthine forms a crystalline dibromide, decomposing at 100° (T., 1914, **105**, 2217). As would be expected, the dichloride is a much more stable compound and is unchanged at 100°. It is almost insoluble in acetone, and can therefore readily be separated from triphenylbismuthine dichloride. The separation of triphenylbismuthine and diphenyl-α-naphthylbismuthine (T., 1921, **119**, 921) by crystallisation from chloroform–alcohol is extremely tedious, and much better results are obtained by treating the mixture with chlorine and separating the two dichlorides, from which the bismuthines may be regenerated by treatment with ammonium sulphide (Michaelis and Marquardt, *loc. cit.*). This is of interest, since it shows that, at the moment of liberation from its dichloride, diphenyl-α-naphthylbismuthine has no tendency to break down to triphenylbismuthine and tri-α-naphthylbismuthine.

Although bismuth trichloride forms crystalline and moderately stable compounds with diazonium chlorides, they do not appear to be strictly analogous to the antimony compounds described by May (T., 1912, **103**, 1037), analyses not agreeing very closely with any simple formulæ. The product obtained from bismuth trichloride and benzenediazonium chloride appears to be represented by the formula $BiCl_3,2PhN_2Cl$ with between 1 and 3 mols. of water of crystallisation. The compounds obtained from *p*-toluene-, and

α- and β-naphthalene-diazonium chlorides are rather more stable at 100° than the phenyl derivative. The behaviour of these compounds towards alkalis is under investigation.

EXPERIMENTAL.

Triphenylbismuthine Difluoride.

Triphenylbismuthine dichloride * (10 grams) and potassium fluoride (3·4 grams) were boiled with 150 c.c. of alcohol and a trace of water. After one and a half hours, the solvent was removed and the residue extracted with hot water. The product thus obtained contained unchanged dichloride. The treatment with potassium fluoride (3 grams) and alcohol was therefore repeated, yielding a solid, which gave no precipitate with alcoholic silver nitrate and, on crystallisation from chloroform–light petroleum and from acetone, melted at 158·5—159° (Found: Bi = 43·26, 43·41; F = 7·77, 7·84. $C_{18}H_{15}F_2Bi$ requires Bi = 43·52; F = 7·95 per cent. $C_{18}H_{16}OFBi$ requires Bi = 43·87; F = 4·01 per cent.).

Estimation of Fluorine in the Difluoride.—The substance was heated for half an hour with excess of calcium oxide and water, containing a little alcohol. (The addition of a small quantity of sodium or calcium carbonate facilitates the subsequent filtration.) The precipitate was washed with alcohol to remove triphenylbismuthine, and ignited. The residue was covered with dilute acetic acid, evaporated to dryness, washed with dilute acetic acid, and the calcium fluoride weighed.

Triphenylbismuthine difluoride is readily soluble in acetone, chloroform, and ether, less so in light petroleum.

The crystals obtained from acetone solution belong to the monoclinic system (class—holohedral, type—digonal equatorial). Measurements of three crystals give the axial ratios $a:b:c$ = 2·0201 : 1 : 1·1163 and the axial angle β = 85° 42′.†

When boiled with barium or calcium oxide in aqueous suspension, the difluoride gives triphenylbismuthine. With sulphuric acid, hydrogen fluoride is liberated.

On boiling the difluoride with 50 per cent. aqueous alcohol for fourteen hours, it was recovered unchanged. A trace of an insoluble powder (0·02 gram), containing bismuth and fluorine, was also obtained.

*

tained When the dichloride was evaporated to dryness three times with aqueous details. fluoric acid, almost the whole was recovered unchanged.

very poor We are much indebted to Sir Henry A. Miers, F.R.S., for his kind interest tri-α-napht preliminary measurements.

Action of Magnesium Phenyl Bromide on Triphenylbismuthine Difluoride.

An ethereal solution containing 3·7 grams (2·6 mols.) of the Grignard reagent was added to 3·7 grams of the difluoride. A vigorous reaction ensued and a brilliant violet colour,* which slowly changed to yellow, was produced. The mixture was heated for one and a half hours and the clear solution decanted. The residue, after magnesium salts had been removed with ammonium chloride, contained bismuth and halogen.

The ether washings and solution were rapidly distilled, and the distillate again evaporated, when one drop of a colourless liquid remained. Judging from the colour produced on treatment with nitric acid, *d* 1·485, this was probably fluorobenzene.

The residue, from the first distillation, on crystallisation from light petroleum and from alcohol, gave 0·9 gram of triphenylbismuthine.

Distillation of Triphenylbismuthine Difluoride.

Twenty grams of the difluoride were distilled in two portions from a small flask, immersed in an oil-bath. The fused mass became turbid at about 200°, and at 226° a white solid was deposited. At 250°, the decomposition became faster and a colourless liquid distilled, whilst at 260° the contents of the flask became black, and rapid distillation of diphenyl was observed. The distillate was separated into three main portions—

(*a*) B. p. 84—88°. 2·6 Grams of fluorobenzene.
(*b*) B. p. 88—110°. A few drops of fluorobenzene.
(*c*) B. p. 235—245°. A few drops of diphenyl, m. p. 70°.

The fluorobenzene fraction was redistilled, b. p. 84—85° (uncorr.). The residue in the flask was repeatedly extracted with hot acetone, leaving a dark mass, containing bismuth and fluorine. The acetone gave an oily solid, from which equal quantities (1 gram) of triphenylbismuthine and diphenyl were isolated.

Action of Potassium Hydrogen Fluoride on Triphenylbismuthine Dichloride.

The dichloride (5·1 grams) and potassium hydrogen fluoride (2 grams) were boiled with aqueous alcohol for three and a half

* This colour is almost always produced when the Grignard reagent interacts with a derivative of quinquevalent bismuth. The possibility of the momentary production of compounds of the type R_5Bi, analogous to the coloured triphenylmethyltetramethylammonium and benzyltetramethylammonium described by Schlenk (*Ber.*, 1916, **49**, 603; 1917, **50**, 274), is not excluded.

hours, and filtered. The residue, on washing with water, gave 0·75 gram of inorganic matter, containing bismuth and fluorine. The alcohol was strongly acid, and deposited a solid which, on extraction with cold light petroleum, gave 2·1 grams of unchanged dichloride and 1·5 grams of triphenylbismuthine.

Action of Potassium Cyanide on Triphenylbismuthine Dichloride.

The dichloride (5·1 grams) and 2·6 grams of potassium cyanide were heated with aqueous alcohol. Some hydrocyanic acid was evolved and, after an hour, the alcohol was evaporated, and warm water added to remove potassium salts. No benzoic acid or benzonitrile was detected in the washings, or in the recovered alcohol. The residue was crystallised from alcohol and then from hot chloroform, giving diphenylcyanobismuthine, m. p. 208°, becoming black at 210° * (Found : CN = 6·55.† $C_{13}H_{10}NBi$ requires CN = 6·70 per cent.).

Action of Potassium Cyanate on Triphenylbismuthine Dichloride.

A. The dichloride (5·1 grams) and 3·2 grams of potassium cyanate were boiled with alcohol for one hour, filtered, and extracted with hot water, when one gram of a solid remained, containing bismuth but no organic matter. The alcohol gave 2·7 grams of triphenylbismuthine.

B. When 2 grams of the dichloride and 0·7 gram of potassium cyanate were shaken for eight and a half hours with 70 c.c. of dry benzene, no reaction occurred.

Diphenylthiocyanobismuthine.

Triphenylbismuthine dichloride (5·1 grams) and lead thiocyanate (6 grams) were boiled with 200 c.c. of alcohol. The mixture became bright yellow, and, after half an hour, the solution was decanted and the solid heated for a further half-hour with more alcohol. The alcoholic extracts had an odour of phenyl thiocyanate. On concentration, a yellow, amorphous powder was obtained resembling the yellow polymerised thiocyanogen, $(SCN)_x$, described by Söderbäck (*loc. cit.*). The filtered solution deposited a solid which, on crystallisation from alcohol and acetone, melted at 122—122·5° (uncorr.) and was quite odourless (Found : S = 7·99, 7·61 ; Bi =

* In another experiment, triphenylbismuthine was also obtained, probably owing to decomposition of some of the cyano-derivative.

† By treatment with excess of standard silver nitrate solution.

49·98; SCN = 13·67.* $C_{13}H_{10}NSBi$ requires S = 7·62; Bi = 49·44; SCN = 13·81 per cent.). The evaporated mother-liquors were distilled in steam. The oily distillate smelled strongly of phenyl thiocyanate, and, with alcoholic potassium hydrosulphide, gave phenyl mercaptan, which was converted to the mercaptides of mercury, lead, and copper. Potassium thiocyanate was recognised in the alkaline solution by the addition of zinc sulphate and ferric chloride.

Diphenylthiocyanobismuthine forms pale yellow crystals, moderately soluble in alcohol and most organic solvents, except light petroleum. It is quite stable when dry, but gradually decomposes in solution, particularly on warming, yielding triphenylbismuthine and a yellow solid, possibly $(SCN)_x$. The yield is therefore low.

The crystals obtained from alcohol belong to the monoclinic system (class—holohedral, type—digonal equatorial). Measurements of three crystals gave the axial ratios $a : b : c = 2{\cdot}4969 : 1 : 3{\cdot}0590$, and the axial angle $\beta = 75°54'$.

Action of Potassium Cyanide on Tri-α-naphthylbismuthine Dichloride.

The dichloride † (1·1 gram), potassium cyanide (1 gram), and alcohol were boiled for two hours, the alcohol evaporated, and the potassium salts removed with water.

The insoluble residue had an odour of naphthalene and, on extraction with chloroform, gave a pale yellow, crystalline solid, m. p. 232°, which did not depress the m. p. of tri-α-naphthylbismuthine. No other organic compounds were isolated.

Action of Potassium Thiocyanate on Tri-α-naphthylbismuthine Dichloride.

The dichloride (1 gram) and potassium thiocyanate (0·4 gram), suspended in benzene, were shaken for eleven hours. The dichloride slowly dissolved, the insoluble matter becoming yellow. The solid was filtered, washed with water and dried, giving 0·45 gram of bismuth salts. The yellow filtrate gave bismuth oxychloride, and

* The thiocyanogen radicle was estimated by dissolving the substance in cold alcohol and diluting to 100 c.c.; 25 c.c. were treated with excess of standard silver nitrate solution, well shaken, heated for a few minutes at 100°, and titrated with ammonium thiocyanate.

† Mixtures of 15, 30, and 60 per cent. of tri-α-naphthylbismuthine, m. p. 235°, and the dichloride, m. p. 167°, melted at 168°, 176°, and 166—205° respectively.

crystals melting at 230—231° and not depressing the m. p. of tri-α-naphthylbismuthine.

Action of Lead Thiocyanate on Tri-α-naphthylbismuthine Dichloride.

Equal weights (5 grams) of these substances were heated with alcohol for eighty minutes, the yellow solid (*a*) separated, heated with more alcohol and filtered, when *tri-α-naphthylbismuthine* was deposited. The alcoholic mother-liquor deposited a red oily mass which, on extraction with light petroleum, yielded *α-naphthyl thiocyanate*, m. p. 55°.

The residue (*a*) was extracted three times with benzene, yielding 2·6 grams of tri-α-naphthylbismuthine, leaving 4·9 grams of a yellow solid, containing bismuth and lead salts, and polymerised thiocyanogen.

No mono- or di-α-naphthylthiocyanobismuthines were isolated.

Action of Thiocyanogen on Tri-α-naphthylbismuthine.

Lead thiocyanate (7·5 grams) was added to a solution of 1 c.c. of bromine in 40 c.c. of dry, alcohol-free ether, the mixture cooled in ice, and shaken for thirty-three minutes, when decolorisation was complete. It was then filtered, and the residue washed with dry ether (60 c.c.), when the solution contained 0·02 gram-mol. of thiocyanogen, $(SCN)_2$. On boiling, or allowing to stand, a yellow polymeride was obtained.

Thirty-four c.c. of the solution were added to 3·93 grams of the bismuthine in dry ether, cooled in ice. The mixture was shaken for five hours, the colour deepening, and, after four hours, the odour of thiocyanogen disappeared. The mixture was filtered and the yellow residue washed with ether. Extraction with boiling benzene removed 2·65 grams of unchanged tri-α-naphthylbismuthine, m. p. 230°; the residue (0·9 gram) appeared to be bismuth thiocyanate.

The ethereal filtrate and washings were evaporated in a vacuum giving an oily, yellow mass which, after two recrystallisations from light petroleum, formed a colourless solid, m. p. 54°. Analysis showed it to be α-naphthyl thiocyanate (Found : S = 17·49, 17·38; C = 71·00; H = 3·82. $C_{11}H_7NS$ requires S = 17·32; C = 71·30; H = 3·81 per cent.).

This, on treatment with alcoholic potassium hydrosulphide and acidification with hydrochloric acid, gave an oil, having the odour of a mercaptan, which gave the respective mercaptides with lead, silver, mercury, and copper salts. Potassium thiocyanate was also detected.

Action of Thiocyanogen on Triphenylbismuthine.

Thirty-four c.c. of the thiocyanogen solution were added to 2·93 grams of the bismuthine in ice-cold ether. Yellow crystals slowly formed on the sides of the vessel but, on shaking for four and a half hours, became oily and were extracted with cold alcohol, yielding 1·7 grams of diphenylthiocyanobismuthine, m. p. 121—122°. The ether was evaporated in a vacuum, the oily residue extracted with cold, dry light petroleum and filtered from 0·8 gram of bismuth thiocyanate and polymerised thiocyanogen. The solution yielded phenyl thiocyanate, which was identified as above.

Action of Potassium Cyanide on Diphenylbromobismuthine.

Diphenylbromobismuthine (2·2 grams) was shaken with 0·6 gram of potassium cyanide in alcohol, containing a small quantity of water, and boiled for a quarter of an hour, when a white, crystalline precipitate was obtained. This was separated, washed with water, dried, and extracted with hot alcohol, leaving a residue of less than 0·05 gram, whilst the alcoholic solutions deposited 1·2 grams of diphenylcyanobismuthine, m. p. 210° (mixed, 210°).

Action of Potassium Fluoride on Diphenylbromobismuthine.

Diphenylbromobismuthine (2·2 grams) was shaken with a cold alcoholic solution of 0·58 gram of potassium fluoride and a few drops of water for five minutes, the solid separated (1·8 grams) and washed with water. Extraction with alcohol yielded 1·9 grams of triphenylbismuthine. The insoluble residue (0·1 gram) contained bismuth and fluorine.

Action of Lead Thiocyanate on Diphenylbromobismuthine.

With diphenylbromobismuthine (1·2 grams) and lead thiocyanate (1·6 grams) in cold alcohol, no reaction was observed. On the next day, the mixture was boiled for one hour, cooled, and filtered. The residue consisted of lead thiocyanate and bromide (probably the double salt, $PbBr_2,Pb(SCN)_2$; Grissom and Thorp, *J. Amer. Chem. Soc.*, 1888, **10**, 229) and bismuth oxybromide. The filtrate gave two deposits—

(*a*) Colourless crystals, m. p. 74—94°.

(*b*) A mixture [illegible] crystals and yellow prisms. These, on fractio[illegible]ohol, yielded triphenylbismuthin[illegible]hine, m. p. 122° (mixed, 122°).

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Action of Silver Nitrate on Diphenylbromobismuthine.

A. Diphenylbromobismuthine (2·2 grams) was shaken with a cold alcoholic solution of silver nitrate (1·5 grams). The white precipitate gradually darkened. After filtering from the residue (probably containing metallic silver) the solution deposited triphenylbismuthine, m. p. 77—78°, on crystallisation from alcohol.

B. Diphenylbromobismuthine (2·2 grams) was added to a boiling alcoholic solution of silver nitrate (0·8 gram). After boiling for an hour, the white precipitate was filtered, and consisted of 0·7 gram of silver bromide and 0·7 gram of bismuth subnitrate.

The evaporated mother-liquor, on successive extractions with hot light petroleum and hot water, yielded 0·3 gram of triphenylbismuthine, m. p. 78°, and unchanged silver nitrate.* The residue was bismuth oxybromide (0·4 gram).

Diphenyl-α-naphthylbismuthine Dichloride.

The bismuthine (2·3 grams), in dry alcohol-free chloroform, was treated with 0·33 gram of chlorine in 6 c.c. of the same solvent, the solution remaining clear. Dry light petroleum was then added until the liquid was turbid, when pale yellow crystals were deposited, m. p. 141—142° (Found: Cl = 12·76, 12·60; Bi = 36·71. $C_{22}H_{17}Cl_2Bi$ requires Cl = 12·64; Bi = 37·07 per cent.).

Diphenyl-α-naphthylbismuthine dichloride is soluble in chloroform, but insoluble in acetone. Moist silver oxide in acetone suspension removes the chlorine atoms, regenerating the bismuthine.

Interaction of Benzenediazonium Chloride and Bismuth Trichloride.

Bismuth trichloride (15 grams) was dissolved in the minimum quantity of hydrochloric acid, and water added until a slight turbidity was produced. A solution of benzenediazonium chloride, prepared from 5 grams of aniline, 30 c.c. of hydrochloric acid, and 75 c.c. of water, was then added and, after a few moments, an orange-yellow, crystalline precipitate was deposited. (No precipitate was obtained on addition of the diazonium solution to bismuth chloride in concentrated hydrochloric acid.) This was filtered, washed quickly with a little of the diazonium solution, and then with a very small quantity of 25 per cent. hydrochloric acid, of-ied on tile for fifteen to twenty minutes, and washed with silver,

detecteden 1·5 grams of silver nitrate were used, some diphenyl was also

dry ether (Found: by Carius's method, Cl = 28·50, 28·34, 28·34; by precipitation, Cl = 27·26, 27·67; Bi * = 31·56, 31·43. $BiCl_3,2PhN_2Cl,1\frac{1}{2}H_2O$ requires Cl = 28·47; Bi = 33·39 per cent. $BiCl_3,2PhN_2Cl,3\frac{1}{2}H_2O$ requires Cl = 26·90; Bi = 31·56 per cent.).

This orange-yellow compound is insoluble in organic solvents and in the diazonium solution, but is easily soluble in water or hydrochloric acid, and readily reacts with aqueous silver nitrate solution. It shows no melting point, but decomposes vigorously at 100°, giving a powerful odour of phenol, which would indicate the presence of water of crystallisation.

The substance gradually decomposes on standing, especially in the presence of light, but not completely after ten days.

Interaction of p-*Toluenediazonium Chloride and Bismuth Trichloride.*

A solution of 15 grams of bismuth trichloride in dilute hydrochloric acid was treated with a solution of toluenediazonium chloride, prepared from 5·3 grams of *p*-toluidine, 15 c.c. of hydrochloric acid, and 50 c.c. of water. The white, crystalline precipitate was filtered and washed as in the last experiment (Found: by Carius's method, Cl = 26·16, 26·08; by precipitation, Cl = 24·72, 24·92; Bi = 22·88, 22·50. $BiCl_3,3C_7H_7N_2Cl,2H_2O$ requires Cl = 26·13; Bi = 25·56 per cent. $BiCl_3,3C_7H_7N_2Cl,8H_2O$ requires Cl = 23·02; Bi = 22·53 per cent.).

Production of a Blue Colouring Matter by the Action of Air and Ammonia on Magnesium Phenyl Bromide.

In preparing triphenylbismuthine from bismuth chloride and magnesium phenyl bromide, the authors have occasionally treated the solid residue, after removal of the ether, with dilute ammonia, with a view to the conversion of diphenylchloro(or -bromo-)-bismuthine (Challenger and Allpress, *loc. cit.*) to triphenylbismuthine. On standing for some days and then distilling in steam to remove diphenyl,† the distillate occasionally had a blue colour, the intensity of which depended on the time the reaction mixture was allowed to stand. The colouring matter was removed hy organic solvents, giving a red solution, which on evaporation had a slight odour of *p*-benzoquinone. Porter and Steele (*J. Amer. Chem. Soc.*, 1920, **42**,

* Determined as sulphide by precipitation in dilute hydrochloric acid solution.

† The bismuthine is more quickly obtained in a pure condition if the distillation with steam is omitted.

2650) have shown that p-benzoquinone and phenol are among the oxidation products of magnesium phenyl bromide, phenol being almost invariably present in any solution of this reagent.* It was then found that similar colorations could be produced by warming a mixture of p-benzoquinone, phenol, and aqueous ammonia.

The authors are again indebted to Messrs. T. Tyrer and Co., Stratford, E., for their assistance, and to the Research Fund of the Chemical Society for a grant, which has partly defrayed the expenses of this investigation.

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XVII.—*Organo-derivatives of Bismuth. Part VI. The Preparation and Properties of Tertiary Aromatic Bismuthines and their Interaction with Organic and Inorganic Halogen Compounds.*

By FREDERICK CHALLENGER and LESLIE RANDAL RIDGWAY.

IN order to determine whether any abnormality of reaction was associated with the halogen-substituted bismuthines, *tri*-p-*chlorophenylbismuthine* and *tri*-p-*bromophenylbismuthine* have been prepared from bismuth chloride and the magnesium derivatives of p-chlorobromobenzene and p-dibromobenzene respectively.

The halogen atoms of tri-p-chlorophenylbismuthine do not react with magnesium phenyl bromide or with ammonia at 160°, and both bismuthines behave normally with chlorine and bromine, giving *dichlorides* and *dibromides*.

As was to be expected, tri-p-chlorophenylbismuthine does not give a di-iodide, *di*-p-*chlorophenyliodobismuthine*, p-chloroiodobenzene, and a red powder containing organic matter and tervalent bismuth being produced (compare Challenger and Allpress, T., 1915, **107**, 21, 23; Michaelis, *Annalen*, 1902, **321**, 164).

The m. p.'s of the dibromides and to a smaller extent the m. p. of tri-p-bromophenylbismuthine dichloride vary with the rate of

* When diphenyl-α-naphthylbismuthine is prepared, and the naphthalene removed by steam distillation, the last portions of the distillate have a strong odour of α-naphthol.

heating. It is interesting to note that almost all bismuthine dibromides melt at about 100—115°.

With moist silver oxide, tri-*p*-chlorophenylbismuthine dichloride and tri-*p*-bromophenylbismuthine dibromide yield the corresponding bismuthines. This is also the case with triphenylbismuthine dibromide and hydroxychloride, and with tri-*p*-tolylbismuthine dibromide (Challenger and Goddard, unpublished observation).

Di-p-*chlorophenylbromobismuthine* was prepared from the corresponding bismuthine and bismuth bromide. With alcoholic ammonia, the bismuthine and bismuth hydroxide are produced, a reaction which is given by all compounds of the types $BiRX_2$ and BiR_2X in presence of bases.

In boiling benzene, di-*p*-chlorophenylbromobismuthine yields the unstable p-*chlorophenyldibromobismuthine*, which is also produced in small quantity from the bismuthine and bismuth bromide, thus :—

$$(C_6H_4Cl)_3Bi + BiBr_3 = (C_6H_4Cl)_2BiBr + C_6H_4Cl\cdot BiBr_2$$
$$2(C_6H_4Cl)_2BiBr = C_6H_4Cl\cdot BiBr_2 + Bi(C_6H_4Cl)_3.$$

Instances of this type of reaction are numerous (Challenger and Allpress, T., 1921, **119**, 917; Challenger, T., 1916, **109**, 250; Grüttner and Wiernik, *Ber.*, 1915, **48**, 1749).

Bismuth chloride and magnesium benzyl chloride in presence of air give bismuth oxychloride and benzaldehyde. A similar reaction is frequently observed with analogous benzyl derivatives; thus tribenzylarsine, when recrystallised from ether, gives benzaldehyde and finally benzoic and arsenic acids (Michaelis and Paetow, *Annalen*, 1886, **233**, 62), whilst from benzyldichloroarsine and water, benzylarsine oxide, arsenious acid, and benzaldehyde are obtained (*ibid.*, p. 91). Tribenzylamine yields toluene and benzaldehyde on distillation or oxidation with bromine water (Limpricht, *Annalen*, 1867, **144**, 307). Benzaldehyde is also formed when tribenzylamine dibromide is decomposed with steam (Wallach, *Annalen*, 1890, **259**, 306. Compare also Smith and Kipping, T., 1912, **101**, 2560).

An attempt to prepare tri-*p*-aminophenylbismuthine by the action of boiling aniline on bismuth chloride was not successful, aniline hydrochloride and diphenylamine being produced (compare Vanino and Hauser, *Ber.*, 1900, **33**, 2271; 1901, **34**, 416).

It has not yet been possible to prepare additive compounds of tertiary bismuthines with alkyl haloids, although the corresponding arsine and stibine derivatives are well defined.

The action of benzyl chloride on triphenylbismuthine was first investigated by Michaelis and Marquardt (*Annalen*, 1889, **251**, 323), who isolated no definite product. The authors find that at

room temperature the mixture reacts vigorously on standing, hydrogen chloride and diphenylmethane being produced. Tri-α-naphthylbismuthine also reacts violently with benzyl chloride, yielding hydrogen chloride, bismuth chloride, a trace of stilbene, and fluorescent products of high b. p., which have not been identified.

It was of interest to determine whether additive compounds were produced from tertiary bismuthines and acid chlorides, but in all instances examined the production of compounds of the types BiR_2X and $BiRX_2$ and a ketone was observed.

	Acid chloride.	Products.
Triphenylbismuthine.	Acetyl chloride.	Acetophenone and diphenylchlorobismuthine.
,,	Benzoyl ,,	Benzophenone and diphenylchlorobismuthine.
Tri-*p*-tolylbismuthine.	Acetyl ,,	*p*-Tolyldichlorobismuthine (Challenger and Allpress, T., 1921, **119**, 917). Ketone not isolated in sufficient quantity.
Triphenylstibine.	Benzoyl ,,	No action.

These results are in close agreement with those of Waga (*Annalen*, 1894, **282**, 323), who treated magnesium diphenyl with acid chlorides.

Triphenylbismuthine and alcoholic mercuric chloride give mercury phenyl chloride (Gillmeister, *Ber.*, 1897, **30**, 2844). It seemed probable that the bismuth oxychloride also isolated arose from diphenylchlorobismuthine produced and decomposed thus:

$$BiPh_3 + HgCl_2 = BiPh_2Cl + HgPhCl;$$
$$BiPh_2Cl + H_2O = BiOCl + 2C_6H_6.$$

This has now been proved to be the case, diphenylchlorobismuthine and mercury phenyl chloride being produced in dry ethereal solution. It was not possible to decide with certainty whether an additive product, $Ph_3Bi,HgCl_2$, was primarily formed.

Triphenylstibine and alcoholic mercuric chloride give no additive product, but form mercury phenyl chloride, antimony trichloride, mercurous chloride, and triphenylstibine dichloride. The three tritolylstibines form additive products, of which the *o*-derivative is stable, whilst with alcohol the *m*- and *p*-isomerides give the corresponding mercuric tolyl chlorides (Michaelis and Genzken, *Annalen*, 1887, **242**, 164 *et seq.*).

This phenylating action of triphenylbismuthine seems further exemplified by its behaviour with silver nitrate (Challenger and Allpress, T., 1921, **119**, 916). These results led to a study of the reactions between *triphenylbismuthine and the chlorides of tervalent* arsenic, antimony, and phosphorus, and this has shown that double decomposition occurs to a certain extent in all cases, the phenyl radicle passing from bismuth to arsenic, antimony, and phosphorus,

the halogen travelling in the opposite direction. These results and some others having a bearing on the question may conveniently be summarised.

*Interaction of Organo-metallic Compounds with Inorganic Halogen Derivatives.**

			Products.
1	Ph_3Bi	PCl_3	Ph_2BiCl; $PhPCl_2$; Ph_2PCl.
2	,,	$AsCl_3$	Ph_2BiCl; $PhAsCl_2$; Ph_2AsCl.
3	,,	$SbCl_3$	Ph_2BiCl; Ph_3SbCl_2.
4	,,	$BiCl_3$	Ph_2BiCl.
5	,,	$HgCl_2$	Ph_2BiCl; $HgPhCl$.
6	,,	$TlCl_3$	Ph_2BiCl; Ph_2TlCl.†
7	,,	$CuCl_2$	Ph_2BiCl; Cu_2Cl_2. No Ph_3BiCl_2.
8	,,	$AgNO_3$	Probably $AgNO_3,2AgPh$.
9	$(C_{10}H_7)_3Bi$	$AsCl_3$	$(C_{10}H_7)_2AsCl$; $BiOCl$ and $C_{10}H_8$ (from $C_{10}H_7\cdot BiCl_2$?).
10	$SbPh_3$	$BiCl_3$	$SbPh_3Cl_2$; Bi_2Cl_4 (?).
11	,,	$TlCl_3$	$SbPh_3Cl_2$; $TlCl$.†
12	,,	$CuCl_2$	$SbPh_3Cl_2$; Cu_2Cl_2 (Michaelis and Reese, *Annalen*, 1886, **233**, 49).
13	$AsPh_3$	$BiCl_3$	Probably forms additive product. No Ph_2BiCl isolated. Odour of phenyl halogen arsines. None isolated.
14	NPh_3	$BiBr_3$	Green solid. Water regenerates NPh_3 and forms $BiOCl$. No other action.
15	$HgPh_2$	$BiBr_3$	$HgPhBr$; $BiPh_3$.
16	,,	$SbCl_3$	$HgPhCl$; $SbPh_3Cl_2$; $SbPh_2Cl_3$ (Hasenbäumer, *Ber.*, 1898, **31**, 2911).

* These reactions were usually carried out at room temperature in ethereal solution, but occasionally other solvents were employed.

† Private communication from Mr. A. E. Goddard.

The tendency of antimony to pass into the quinquevalent condition (compare Michaelis and Reese, *Annalen*, 1886, **233**, 45) is illustrated by reactions 3, 10, 11, 12, and 16. It is possible that reaction 10 is analogous to 12, giving bismuth dichloride, Bi_2Cl_4 (Schneider, *Pogg. Ann.*, 1855, **96**, 130; Weber, *ibid.*, 1859, **107**, 596). The contrast between reactions 2 and 3 is very striking. Reaction 14 is probably analogous to the production of dark green or blue compounds from tertiary aromatic amines and the pentachlorides of phosphorus and antimony (Wieland, *Ber.*, 1907, **40**, 4279).

Whilst the transfer of a phenyl group from nitrogen to bismuth seems impossible, only slightly better results were obtained with bismuth chloride and triphenylarsine, from which it would appear that the course of reactions of this type is not solely determined by considerations of solubility. This conclusion is strengthened by the fact that whilst the phenyl group can be easily transferred from mercury to phosphorus, arsenic, antimony, or bismuth, triphenylphosphine and triphenylarsine have little or no tendency to

convert mercuric chloride to mercury phenyl chloride, although the analogous stibine and bismuthine readily do so.

In the reactions here described the migration of phenyl groups from one element to another occurs in the presence of a halogen atom. Schlenk and Holtz (*Ber.*, 1917, **50**, 262) describe the production of the sparingly soluble lithium methyl by interaction of lithium ethyl and mercury dimethyl in benzene–light petroleum at the ordinary temperature. Lithium phenyl was similarly prepared by the use of mercury diphenyl in benzene solution.

So far as the authors are aware, no other reactions of this type have been recorded among organo-metallic compounds.* Accordingly, mercury diphenyl and tri-α-naphthylbismuthine were heated in benzene solution, but mercury di-α-naphthyl was not detected. *At 200°, however, in the absence of a solvent, an interchange of* groups was found to occur, mercury di-α-naphthyl, triphenylbismuthine, and diphenyl-α-naphthylbismuthine being obtained.

Tri-*p*-tolylbismuthine and mercury diphenyl at 180° similarly gave rise to mercury di-*p*-tolyl, but under the same conditions tri-*p*-tolylbismuthine and mercury di-α-naphthyl were unchanged. It would thus appear that the α-naphthyl group has a greater affinity for mercury than the phenyl or *p*-tolyl group. This is confirmed by our observation that mercury di-α-naphthyl is produced by the action of magnesium α-naphthyl bromide on mercury phenyl bromide, presumably according to the equation $2C_{10}H_7{\cdot}MgBr + HgPhBr = Hg(C_{10}H_7)_2 + MgPhBr + MgBr_2$, and not by the decomposition of the unknown mercury α-naphthylphenyl, $2C_{10}H_7{\cdot}HgPh = Hg(C_{10}H_7)_2 + HgPh_2$, since only traces of mercury diphenyl could be detected (compare Hilpert and Grüttner, *loc. cit.*).

A most interesting example of this type of reaction is afforded by the ready production of diphenyl-α-naphthylbismuthine by the fusion of tri-α-naphthylbismuthine and triphenylbismuthine at 190°. The extension of this method to the preparation of other mixed bismuthines is under investigation. A preliminary experiment appeared to indicate that this reaction is reversible. No interaction was observed between tri-α-naphthylbismuthine and tri-*p*-tolylarsine at 200°.

EXPERIMENTAL.

Tri-p-*chlorophenylbismuthine.*

An ethereal solution of magnesium *p*-chlorophenyl bromide prepared from *p*-chlorobromobenzene (50 grams), magnesium

* Apart from the work of Frankland on the methyl and ethyl derivatives of zinc and mercury (*Annalen*, 1859, **111**, 57. Compare Hilpert and Grüttner, *Ber.*, 1915, **48**, 906)

(6·3 grams), and iodine (0·5 gram) was treated with 24·6 grams of bismuth chloride in dry ether. A vigorous reaction took place, a yellow solid being deposited. The ether was removed, the mixture heated at 100° for four hours, treated with water, halogenobenzenes and any diphenyl derivatives were removed in steam, and the filtered residue was extracted with acetone. The solution deposited a colourless solid, which, on crystallisation from a mixture of ethyl acetate and acetone, melted at 116° (Found: Bi = 38·21, 38·19; Cl = 19·79, 19·78. $C_{18}H_{12}Cl_3Bi$ requires Bi = 38·34; Cl = 19·61 per cent.).

Tri-*p*-chlorophenylbismuthine is easily soluble in most organic solvents, but sparingly so in alcohol or light petroleum. With hydrochloric acid, chlorobenzene is produced.

When heated for several hours with 1 mol. of magnesium phenyl bromide, the ether distilled, and the residue, after three hours at 100°, decomposed with water, only unchanged bismuthine, diphenyl and bismuth oxybromide (0·1 gram) were isolated.

When the bismuthine (2 grams) was heated with concentrated alcoholic aqueous ammonia for five hours at 100° or at 160° in a sealed tube for four hours, 1·9 grams were recovered unchanged and no ammonium chloride was formed.

Tri-*p*-chlorophenylbismuthine dichloride was prepared from the bismuthine and chlorine in chloroform–light petroleum solution, and on crystallisation from the same solvents formed a colourless solid, m. p. 141°, readily soluble in chloroform or benzene, but sparingly so in light petroleum. The yield was almost quantitative (Found: Bi = 33·39; Cl = 28·68. $C_{18}H_{12}Cl_5Bi$ requires Bi = 33·91; Cl = 28·90 per cent.). After one hour at 100° the dichloride did not smell of chlorobenzene and melted at 138°.

Two grams of the dichloride and 0·75 gram of silver oxide were suspended in moist acetone, after two days the mixture was filtered, and the residue extracted with etbyl acetate, yielding 1·2 grams of tri-*p*-chlorophenylbismuthine (m. p. 115°).

Tri-*p*-chlorophenylbismuthine dibromide was similarly prepared and crystallised from chloroform–light petroleum; m. p. 105° (Found: Bi = 29·33 per cent.; AgCl + AgBr = 0·2063 gram. $C_{18}H_{12}Cl_3Br_2Bi$ requires Bi = 29·61 per cent.; AgCl + AgBr = 0·2053 gram). It forms colourless crystals, the m. p. varying with the rate of heating. After a few minutes at 100°, the odour of a dihalogenated benzene is apparent.

*Action of Iodine on Tri-*p*-chlorophenylbismuthine.*

When 1 gram of the bismuthine was gradually treated with 0·47 gram of iodine, both in ether–chloroform solution, a red precipitate

(0·2 gram) was produced and the temperature rose slightly. After filtration in absence of moisture and evaporation to a small bulk, light petroleum precipitated a yellow solid (0·5 gram), m. p. 113° (Found: AgCl + AgI = 0·2159. $C_{12}H_8Cl_2IBi$ requires AgCl + AgI = 0·2164 gram).

Di-*p*-chlorophenyliodobismuthine dissolves easily in chloroform or ether. On recrystallisation from chloroform–light petroleum, dry solvents (free from alcohol) being used, a red solid containing organic matter and readily soluble in most solvents was deposited with the yellow crystals, which then melted at 139°.

When the mother-liquors and washings were evaporated, the solidified residue, on treatment with hot water, gave bismuth oxyiodide and an oil which, with light petroleum, yielded *p*-chloroiodobenzene (m. p. 56°). This was treated with chlorine in chloroform solution, giving *p*-chloroiodobenzene dichloride (m. p. 110° [decomp.]).

The original red precipitate contained organic matter and turned black at 150°, but did not melt. With hydrochloric acid, halogenobenzene was liberated.

Di-p-*chlorophenylbromobismuthine and* p-*Chlorophenyldibromobismuthine.*

Tri-*p*-chlorophenylbismuthine (3 grams; 2 mols.) in dry ether was treated with a similar solution of bismuth bromide (1·24 grams; 1 mol.), when some bismuth oxybromide was precipitated and removed. On concentration in a vacuum, colourless crystals and a trace of yellow solid separated.

The colourless substance, when crystallised from ether, melted at 159° (Found: Br = 15·95, 15·84;* Bi = 40·52, 40·61. $C_{12}H_8Cl_2BrBi$ requires Br = 15·64; Bi = 40·70 per cent.).

Di-*p*-chlorophenylbromobismuthine is easily decomposed by water and moist solvents. When warmed with alcoholic ammonia, the bismuthine is regenerated. Its solution in hot dry benzene deposits a yellow solid, m. p. 244° (Found: Br = 33·26, 33·11;* Bi = 43·41, 43·36 per cent.; AgCl + AgBr = 0·1797 gram. $C_6H_4ClBr_2Bi$ requires Br = 33·35; Bi = 43·39 per cent.; AgCl + AgBr = 0·1809 gram).

p-Chlorophenyldibromobismuthine is only slightly soluble in hot benzene or hot chloroform, and almost insoluble in all other solvents. It decomposes on standing for a few hours.

* Reactive bromine estimated volumetrically by means of silver nitrate solution.

*Tri-*p*-bromophenylbismuthine.*

The solution of magnesium *p*-bromophenyl bromide (3 mols.) prepared from 60 grams of *p*-dibromobenzene, 6·1 grams of magnesium, 200 c.c. of dry ether, and 0·5 gram of iodine, which had an intense bluo colour, was vigorously stirred and slowly treated with an ethereal solution of 26·6 grams (1 mol.) of bismuth chloride. A green solid was deposited, the ether removed, the residue heated at 100° for four hours, decomposed with water, and distilled with steam to remove hromobenzene and any dibromodiphenyl. The filtered residue was extracted three times with acetone, which on concentration deposited a viscous, brown oil. After prolonged treatment with acetone, chloroform, and alcohol, this became solid and was crystallised from a mixture of acetone and ethyl acetate, when it formed a white, granular powder, m. p. 149° (Found: Bi = 30·67, 30·73; Br = 35·23, 35·34. $C_{18}H_{12}Br_3Bi$ requires Bi = 30·77; Br = 35·49 per cent.).

Tri-*p*-bromophenylbismuthine is very soluble in ether, chloroform, acetone, or ethyl acetate, less so in light petroleum or alcohol, and with hydrochloric acid yields bromobenzene.

An experiment performed with 4·5 molecules of the Grignard reagent yielded, in addition to the bismuthine, a small quantity of white solid, m. p. 220° on recrystallisation from ethyl acetate. This awaits investigation (compare Lederer, *Ber.*, 1916, **49**, 2004).

Tri-*p*-bromophenylbismuthine dichloride was prepared as usual (see p. 109) and on crystallisation from dry chloroform–light petroleum melted at 155° (Found: Bi = 27·79 per cent.; AgCl + AgBr = 0·1984 gram. $C_{18}H_{12}Cl_2Br_3Bi$ requires Bi = 27·85 per cent.; AgCl + AgBr = 0·1982 gram). It forms white, matted crystals readily soluble in chloroform, benzene, or acetone, insoluble in light petroleum. The m. p. varied slightly, the same specimen melting at 151°, 153°, and 155° when the rate of heating was altered.

Tri-*p*-bromophenylbismuthine dibromide was obtained from the bismuthine and bromine in chloroform–light petroleum solution, and on crystallisation from dry henzene–light petroleum formed a faintly yellow solid, m. p. 107° (decomp.). When heated at 100°, the odour of dibromobenzene was very pronounced (Found: Bi = 24·86; Br = 48·09. $C_{18}H_{12}Br_5Bi$ requires Br = 47·81; Bi = 24·88 per cent.).

On shaking 2 grams of the dibromide, 0·56 gram of silver oxide, and 15 c.c. of acetone, a reaction quickly occurred. The acetone filtrate had a very pungent and lachrymatory odour, and was concentrated in a current of air. This removed the irritant, and tri-

p-bromophenylbismuthine was deposited together with a trace of unchanged dibromide (m. p. 98°).

Interaction of Bismuth Chloride and Magnesium Benzyl Chloride.

On addition of 11·2 grams of bismuth chloride (1 mol.) in dry ether to an ethereal solution of 3 mols. of magnesium benzyl chloride (2·8 grams of magnesium; 15·0 grams of benzyl chloride), a yellow precipitate was deposited. Water was added and the ether separated and distilled, yielding only dibenzyl. The precipitate, on extraction with alcohol, gave a yellow solution, which decomposed in air, bismuth oxychloride and benzaldehyde being produced. The latter was removed in steam, and converted into its semicarbazone, which melted at 212° and did not depress the m. p. of pure benzaldehydesemicarbazone.

The residue from the steam distillation, on extraction with alcohol, yielded an oil which contained no bismuth and did not decolorise a solution of bromine in chloroform.

Action of Aniline on Bismuth Chloride.

Ten grams (1 mol.) of bismuth chloride and 18 grams (6 mols.) of aniline were heated for thirty-five hours at 190°, forming a viscous mass. Hot water removed 6 grams of aniline as hydrochloride, and a blue solid remained which dissolved readily in alcohol, leaving bismuth oxychloride. From the alcohol, by evaporation and extraction with light petroleum, a small quantity of diphenylamine (m. p. 52°) was isolated, together with unchanged aniline. The residue contained all the colouring matter, melted above 200°, and was free from bismuth. On treatment with solvents, nothing further was isolated.

Action of Acetyl Chloride on Triphenylbismuthine.

When the bismuthine (8·5 grams) was treated with 1·52 grams of acetyl chloride in carbon tetrachloride, a vigorous reaction took place, but no hydrogen chloride was liberated. The solution was boiled for four hours, when it became yellow and deposited a brown precipitate. The liquid, still containing acetyl chloride, was decanted and the precipitate (*m. p. 175°*) washed with light petroleum …d extracted with dry benzene, which removed some inorganic …er. The filtrate, on addition of light petroleum, deposited …ylchlorobismuthine.

…nother-liquor and washings yielded a yellow oil which

solidified at 0°. This was treated with hot, dilute hydrochloric acid to remove bismuth compounds, washed with water, and poured into a hot aqueous solution of semicarbazide hydrochloride and sodium acetate, when acetophenonesemicarbazone (m. p. 195°) was deposited on cooling; the pure product melted at 198°.

Action of Benzoyl Chloride on Triphenylbismuthine.

The bismuthine (5·5 grams; 1 mol.), benzoyl chloride (1·77 grams; 1 mol.), and carbon tetrachloride (15 c.c.) were heated for six hours, until the odour of benzoyl chloride disappeared. Extraction with chloroform and light petroleum gave a grey solid, which was recrystallised from dry benzene–light petroleum, colourless crystals (m. p. 183°) being obtained. These did not depress the m. p. of diphenylchlorobismuthine and with ammonia formed triphenylbismuthine (see p. 105).

The chloroform–petroleum extracts yielded an oil which on treatment with dilute hydrochloric acid gave a viscous solid. This, when dried and washed with light petroleum, formed pale yellow crystals (m. p. 47°) resembling benzophenone in odour. With hydroxylamine hydrochloride these yielded crystals, m. p. 140°, not depressing the m. p. of benzophenoneoxime.

*Action of Acetyl Chloride on Tri-*p*-tolylbismuthine.*

No reaction took place in the cold when the bismuthine (2 grams; 1 mol.) and acetyl chloride (0·5 gram; 2 mols.) were mixed in carbon tetrachloride solution. After four hours on the water-bath, the cold solution deposited a white solid (1·4 grams; m. p. 179°) and a small quantity of a yellow substance (m. p. 200°). The deposit was recrystallised from cold dry chloroform–light petroleum, giving di-*p*-tolylchlorobismuthine (m. p. 180°) (Found: Bi = 48·75; Cl = 8·30. $C_{14}H_{14}ClBi$ requires Bi = 48·88; Cl = 8·33 per cent.).

The mother-liquors and washings were united and heated for five hours, yellow crystals (m. p. 206°), which were almost certainly *p*-tolyldichlorobismuthine (m. p. 206°), being deposited.

The supernatant liquid was decanted and distilled in steam, giving traces of a colourless oil which had a strong, aromatic odour, but did not react with semicarbazide hydrochloride.

Benzoyl Chloride and Triphenylstibine.

The stibine (3 grams) and benzoyl chloride (1·2 grams) were boiled with carbon tetrachloride for four hours. No reaction

occurred even after removing the solvent and heating for four hours at 100°. Much benzoyl chloride remained unchanged, and on treatment with chlorine 2·5 grams of stibine were recovered as dichloride (3 grams).

Phosphorus Trichloride and Triphenylbismuthine.

The bismuthine (5 grams) was treated with phosphorus trichloride (1·6 grams), both in dry ether, colourless crystals being immediately deposited, which, on crystallisation, melted at 183° and did not depress the m. p. of diphenylchlorobismuthine.

The ether yielded a yellow, viscid oil (*A*) containing halogen but no bismuth. A portion solidified on treatment with chlorine in a freezing mixture; the product, m. p. 64°, fumed in air, rapidly changing to a viscous liquid and was in all probability crude phosphenyl tetrachloride (m. p. 73°). The oil (*A*) similarly gave an unstahle solid when treated with bromine at 0°. The presence of phenyldichlorophosphine (phosphenyl chloride) was further shown by conversion of (*A*) into phenylphosphinous acid, $PhP(OH)_2$. The oil was dropped slowly into ice-water, immediate reaction taking place. The mixture was boiled and rapidly filtered. The solution, on concentration in a stream of carbon dioxide, deposited a white solid, m. p. 68°. Phenylphosphinous acid melts at 70°.

A boiling aqueous solution of the acid reduced mercuric chloride to mercurous chloride. The phenylphosphinic acid, $PhPO(OH)_2$, formed in this way was not isolated.

Arsenic Trichloride and Triphenylbismuthine.

To 8 grams (1 mol.) of the bismuthine in dry ether 3·3 grams of arsenic trichloride in the same solvent were slowly added. In the course of ten minutes 7·2 grams of colourless crystals were deposited which, washed with dry ether and recrystallised from dry benzene–light petroleum, melted at 183°, contained halogen, but no arsenic, and did not depress the m. p. of diphenylchlorobismuthine (Found: Bi = 52·55. $C_{12}H_{10}ClBi$ requires Bi = 52·32 per cent.). From the ethereal solution a pale yellow, viscid oil (containing halogen but no bismuth) was isolated. This had a very pungent odour and a destructive action on the skin. It was fluid below 0° and stable to water, but with dry chlorine at 0° gave a yellow solid, m. p. 40° (not sharp). This was probably phenylarsenic chloride, $C_6H_5{\cdot}AsCl_4$, m. p. 45° (La Coste and Michaelis, *Annalen*, 1880, **201**, 191).

The bulk of the oil, in aqueous suspension, was treated with chlorine for some hours, boiled, and filtered. The solution deposited

white crystals, which decomposed at 157°, gave silver and copper salts, and were doubtless phenylarsinic acid. The yellow oil must therefore have contained phenyldichloroarsine.

In a second experiment, the mixture remained for twelve hours after the deposition of diphenylchlorobismuthine (m. p. 184°), when a yellow, unstable solid, sparingly soluble in hot benzene, was precipitated. It contained organic matter and melted above 185°, but could not be purified.

The ethereal solution was decanted and evaporated. The residual oil was suspended in water, treated with chlorine, boiled, and cooled, when diphenylarsinic acid, m. p. 174°, was deposited. The barium salt was analysed (Found : Ba = 20·86. $C_{24}H_{20}O_4As_2Ba$ requires Ba = 20·83 per cent.). The yellow oil therefore contained diphenylchloroarsine. Probably both experiments gave a mixture of the chloroarsines.

Antimony Trichloride and Triphenylbismuthine.

One gram (1 mol.) of antimony trichloride in dry ether was added to 2 grams (1 mol.) of the bismuthine in the same solvent, when a white precipitate consisting largely of inorganic compounds of bismuth and antimony was produced. The decanted ether deposited bismuth oxychloride, but on concentration gave a solid, m. p. 140°, containing chlorine and antimony, but no bismuth. This on crystallisation from chloroform–light petroleum did not depress the m. p. of triphenylstibine dichloride. When evaporated with aqueous alcohol and crystallised from benzene, triphenylstibine hydroxychloride (m. p. and mixed m. p. 217°) was obtained.*

A chloroform extract of the first deposit yielded more triphenylstibine dichloride and also diphenylchlorobismuthine (m. p. 184°), which was further characterised by conversion to triphenylbismuthine with ammonia.

Bismuth Trichloride and Triphenylstibine.

Bismuth trichloride (7·7 grams; 1 mol.) was slowly added to the stibine (8·6 grams; 1 mol.), both in dry ether. The first few drops produced a transient, brown coloration and a permanent, yellow precipitate, containing inorganic compounds of bismuth and antimony.

* It is interesting that the m. p. of a mixture of triphenylstibine dichloride and triphenylbismuthine dichloride is only four degrees lower than that of the pure triphenylstibine dichloride (m. p. 143°). The m. p.'s taken simultaneously were : Triphenylstibine dichloride = 143°. Mixture = 139°. Triphenylbismuthine dichloride = 139°.

On the next day, the ether was decanted, evaporated in absence of moisture, and the yellow, semi-solid residue extracted with light petroleum, which discharged the colour. The extract deposited triphenylstibine dichloride, m. p. 142°, which was converted to the hydroxychloride (m. p. 217°; mixed, 217°).

The mother-liquors and the original solution gave no trace of any organic bismuth compound.

Arsenic Trichloride and Tri-α-naphthylbismuthine.

Three grams of the bismuthine in a mixture of dry benzene and dry chloroform were treated with 0·93 gram of arsenic trichloride in dry ether. During fifteen hours, a dark solid free from organic matter and containing arsenic was deposited and the yellow solution became green. The decanted mother-liquor was evaporated spontaneously in absence of moisture, yielding di-α-naphthylchloroarsine, m. p. 167° (Matsumiya, *J. Tōkyō Chem. Soc.*, 1920, **41**, 868) (Found : Cl = 9·57; As = 20·49. $C_{20}H_{14}ClAs$ requires Cl = 9·72; As = 20·56 per cent.).

Bismuth oxychloride and naphthalene (m. p. 80°; picrate, m. p. 148°) were produced at the same time, probably as decomposition products of α-naphthyldichlorobismuthine.

The dark solid was insoluble in chloroform or benzene. Dry ether extracted bismuth chloride.

Bismuth Tribromide and Triphenylamine.

With bismuth bromide (5·5 grams; 1 mol.) and triphenylamine (3·0 grams; 1 mol.), both in dry ether, a dark green solid was deposited. On the next day, some of the solvent was removed, when triphenylamine (m. p. 125°; mixed, 125°) was recovered. The whole of the ether was then evaporated and water added. This discharged the colour, only bismuth oxybromide and triphenylamine (m. p. 126°) being isolated.

Bismuth Trichloride and Triphenylarsine.

(*a*) Bismuth trichloride (7 grams; 1 mol.) in dry ether was slowly added to an ethereal solution of the arsine (6·8 grams; 1 mol.). No precipitate was formed, but the solution on evaporation deposited a yellow, viscous solid. This with cold light petroleum and with benzene yielded triphenylarsine, m. p. 59° on recrystallisation. The crude arsine contained traces of a halogen compound (copper-wire test) and had the odour of a phenylchloroarsine, but no such

substance was isolated. A portion of the yellow residue was treated with water, when all colour was discharged. Extraction with chloroform then gave bismuth oxychloride and triphenylarsine (m. p. 58°) containing traces of halogen. The remainder of the oil was decomposed with ammonia, and extracted with alcohol, triphenylarsine (m. p. 53°; recrystallised, 58°) being obtained. Treatment of the crude arsine with hydrochloric acid and hydrogen sulphide yielded a trace of bismuth sulphide, indicating the probable presence of traces of triphenylbismuthine, arising from diphenylchlorobismuthine and ammonia (see p. 105).

(*b*) Bismuth chloride (5·1 grams) and the arsine (5 grams) were boiled with toluene. After six hours the solution became yellow and, on cooling, deposited colourless, hygroscopic crystals (m. p. 80—90°), becoming yellow in air. These were probably a double compound of the arsine and bismuth chloride, since with water only triphenylarsine and bismuth oxychloride were obtained.

The mother-liquor was evaporated and treated with ammonia; careful fractionation yielded only triphenylarsine (m. p. 59°). A slight odour of a phenylchloroarsine was observed, but no such compound or any triphenylbismuthine was isolated.

The Action of Hydrated Cupric Chloride on Triphenylbismuthine.

The bismuthine (2 grams), cupric chloride (1·55 grams; 2 mols.), and alcohol (20 c.c.) were vigorously shaken together. The solution was decolorised in fifteen minutes and the theoretical quantity (0·9 gram) of cuprous chloride precipitated. The filtered solution, when evaporated at room temperature, gave three deposits of diphenylchlorobismuthine (m. p. 183°, 183°, 179°). The last was washed with chloroform, but the extract contained no triphenylbismuthine dichloride. Similar results were obtained in chloroform solution. This reaction is being further investigated with a view to the isolation of an organo-copper compound.

Interaction of Mercuric Chloride and Triphenylbismuthine.

Mercuric chloride (1·85 grams; 1 mol.) was added to triphenylbismuthine (3 grams; 1 mol.), both in dry ether. A solid, m. p. 164°, was at once precipitated, which was dissolved in a large volume of cold dry benzene. Addition of light petroleum gave mercury phenyl chloride, m. p. 250°. The mother-liquor yielded diphenylchlorobismuthine (m. p. 183°), which with alcoholic ammonia gave triphenylbismuthine.

A portion of the original ethereal filtrate was concentrated, when

more solid (m. p. 166°) separated. This and the mother-liquor yielded the same products as before. The original precipitate (m. p. 166°),* when treated with hot glacial acetic acid or with water, gave mercury phenyl chloride and inorganic bismuth compounds. The aqueous solution was free from metallic radicles, but contained hydrochloric acid.

Interaction of Triphenylbismuthine and Benzyl Chloride.

The bismuthine was treated with excess of benzyl chloride in dry ether and, after eight weeks at room temperature, a trace of bismuth oxychloride was deposited. On removing the ether, most of the triphenylbismuthine was recovered.

Spontaneous reaction took place when the mixture, free from ether, was left in a desiccator, hydrogen chloride and a brown, oily mass being produced. On extraction with chloroform and light petroleum, bismuth oxychloride remained. The solvent was then evaporated and the residue distilled, when a viscous liquid (b. p. 255—265°) was obtained. This was probably diphenylmethane, since oxidation with chromic acid gave benzophenone, which was isolated as the oxime (m. p. 140°).

Interaction of Tri-α-naphthylbismuthine and Mercury Diphenyl.

The bismuthine (5 grams; 1 mol.) and mercury diphenyl (3 grams; 1 mol.) were boiled for two hours in benzene–chloroform solution, but on fractional crystallisation were recovered unchanged.

The same quantities of the bismuthine and mercury diphenyl were then heated in an oil-bath at 200°. The mixture softened at 180° and melted at 200°. After two and a half hours, it was cooled and extracted with acetone. Practically no inorganic matter remained. The residue was crystallised from benzene, yielding mercury di-α-naphthyl (m. p. 245°; mixed, 243°), which was characterised by conversion to mercury α-naphthyl bromide (m. p. 198°).

The acetone extract yielded an oil, a portion of which was distilled with steam, yielding naphthalene (m. p. 82°). The residue could not be crystallised from any solvent and appeared to be a mixture of triphenylbismuthine and diphenyl-α-naphthylbismuthine. The whole of the acetone-soluble products were therefore dissolved

* Although three deposits, m. p. 164°, 166°, 166°, were obtained, analysis appeared to indicate that the product was not $Bi(C_6H_5)_3,HgCl_2$ nor even an equimolecular mixture of $(C_6H_5)_2BiCl$ and $C_6H_5{\cdot}HgCl$. Production and partial separation of these last-named substances probably occur even in dry ethereal solution.

in chloroform–light petroleum and treated with chlorine (Challenger and Wilkinson, this vol., p. 95), whereby a viscous solid (*A*) was precipitated. The mother-liquors deposited diphenyl-α-naphthylbismuthine dichloride (m. p. 140°; mixed, 139°). This was decomposed with ammonium sulphide (Challenger and Wilkinson, *loc. cit.*) and the product recrystallised from alcohol, giving crude diphenyl-α-naphthylbismuthine (m. p. 113°). The quantity was too small for further purification.

The solid (*A*), on treatment with chloroform and ether, yielded (*a*) a small quantity of mercury phenyl chloride (m. p. 249°), resulting from the action of chlorine on unchanged mercury diphenyl, and (*b*) crude triphenylbismuthine dichloride (m. p. 120°), which with moist silver oxide in acetone yielded triphenylbismuthine (m. p. 76°; mixed, 77°), thereby confirming the presence of this substance in the original fused mixture.

Interaction of Triphenylbismuthine and Tri-α-naphthylbismuthine.

Triphenylbismuthine (5 grams; 2 mols.) and tri-α-naphthylbismuthine (3·4 grams; 1 mol.) were heated at 190° for two hours, cooled, extracted with acetone, and filtered. The residue contained some inorganic bismuth compound together with a little unchanged tri-α-naphthylbismuthine (m. p. 235°). The acetone extract deposited diphenyl-α-naphthylbismuthine (m. p. 112°), which, after several crystallisations from chloroform-alcohol, melted at 118° and was characterised by conversion to the dichloride (m. p. 140°; mixed, 140°). The acetone liquors were evaporated and distilled with steam, whereby naphthalene (m. p. 87°) was removed. The residue was unchanged triphenylbismuthine (m. p. 76°).

*Tri-*p*-tolylbismuthine and Mercury Diphenyl.*

On heating the bismuthine (5 grams; 1 mol.) and mercury diphenyl (3·7 grams; 1 mol.), complete fusion took place at 120°. After one hour the mass became quite solid again at this temperature and only partly melted when kept at 180° for one hour. The cold mixture was extracted with acetone, filtered, and the residue crystallised from benzene, when mercury di-*p*-tolyl (3 grams) was obtained (m. p. 237°). This was converted by bromine in chloroform to mercury *p*-tolyl bromide (m. p. 226°) and *p*-bromotoluene. The acetone mother-liquors deposited a solid (m. p. 88°), which, when recrystallised from acetone, yielded tri-*p*-tolylbismuthine (m. p. 120°; mixed, 120°).

The mother-liquors gave an oil which could not be crystallised.

With chlorine in chloroform–light petroleum solution it yielded mercury phenyl chloride (m. p. 249°), indicating the presence of unchanged mercury diphenyl. The final mother-liquors deposited crystals (m. p. 119—124°), which were probably a mixture of triphenylbismuthine dichloride and tri-*p*-tolylbismuthine dichloride.

Action of Magnesium α-Naphthyl Bromide on Mercury Phenyl Bromide.

Mercury phenyl bromide (8 grams) was gradually added to the Grignard reagent (4 mols.) in benzene–ether solution. Rapid solution occurred, and after half an hour at room temperature the mixture was cooled in ice, decomposed with excess of 1 per cent. sulphuric acid, and filtered. A portion of the benzene solution was evaporated at room temperature, the residue yielding about 3 grams of mercury di-α-naphthyl (m. p. 245°). Since all rise of temperature had been avoided, it appeared very unlikely that this could have been formed by decomposition of mercury α-naphthylphenyl. The remainder of the benzene solution was therefore distilled with steam to remove naphthalene, and crystallised from benzene as before. The mother-liquors finally yielded a small amount of a solid, which on treatment with bromine in chloroform–light petroleum solution gave a trace of mercury phenyl bromide. Another experiment gave similar results.

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XVIII.—*The Aliphatic Sulphonamides. Part I.*

By Percival Walter Clutterbuck and Julius Berend Cohen.

In a paper by Dakin, Cohen, Daufresne, and Kenyon (*Proc. Roy. Soc.*, 1916, [*B*], 89, 232) it was shown that the aromatic chloroamines possess powerful antiseptic properties. These substances were obtained by the action of sodium hypochlorite on the sulphonamides

and have the general formula $Ar\cdot SO_2\cdot NNaCl$ (Ar = aromatic radicle). As benzylsulphonamide reacts in the same fashion as, for example, benzenesulphonamide, and as the benzyl radicle resembles in its general behaviour an alkyl group, it was thought possible to obtain similar products, having a more active antiseptic action weight for weight, from the aliphatic sulphonamides and more especially from the aliphatic disulpbonamides with which the present paper is concerned. Although our expectation has not been realised, for these sulphonamides apparently do not react with sodium hypochlorite, we think, nevertheless, that the results are not without interest. Ethanedisulphonyl chloride was first prepared by Königs (*Ber.*, 1874, **7**, 1163) by tbe action of phosphorus pentachloride on the sodium or potassium salt of the disulphonio acid. In an attempt to obtain the amide, it was found that water, alcohol, aqueous ammonia, or ammonia gas in presence of an inert solvent (ether, benzene, etc.), aliphatic and, as Autenrieth and Rudolph (*Ber.*, 1901, **34**, 3469) have sbown, aromatic bases all liberate sulphur dioxide either in the cold or on warming.

On boiling with water, two reactions occur concurrently, in the proportion of about 90 per cent. of the first to 10 per cent. of the second :

$$1.\ \begin{array}{l}CH_2\cdot SO_2Cl\\ |\\ CH_2\cdot SO_2Cl\end{array} + H_2O = \begin{array}{l}CH_2\\ \|\\ CH\cdot SO_3H\end{array} + 2HCl + SO_2.$$

$$2.\ \begin{array}{l}CH_2\cdot SO_2Cl\\ |\\ CH_2\cdot SO_2Cl\end{array} + 2H_2O = \begin{array}{l}CH_2\cdot SO_3H\\ |\\ CH_2\cdot SO_3H\end{array} + 2HCl.$$

As the product of the action of ammonia gas on the substance dissolved in ether was difficult to isolate in a pure state, the action of aniline was examined. This reaction has been very fully studied by Autenrieth and Rudolph (*loc. cit.*), by Autenrieth and Koburger (*Ber.*, 1903, **36**, 3626), and also by Kohler (*Amer. Chem. J.*, 1897, **19**, 745).

The product obtained by Autenrieth and Rudolph was represented by formula I, whilst Kobler assigned to it formula II.

$$\underset{\text{(I.)}}{\begin{array}{l}CH_2\\ \|\\ CH\cdot SO_2\cdot NH\cdot C_6H_5.\end{array}} \qquad \underset{\text{(II.)}}{\begin{array}{l}CH_2\cdot SO_2\\ |\qquad |\\ CH_2\cdot N\cdot C_6H_5.\end{array}} \qquad \underset{\text{(III.)}}{\begin{array}{l}CH_2\cdot NH\cdot C_6H_5,HCl\\ |\\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5.\end{array}}$$

Kohler at the same time showed tbat whilst the above compound (I or II) is mainly prodnced wben aniline is dropped into the fused sulphonyl chloride, if the reaction proceeds in ether solution at the ordinary temperature the compound III is the main product.

Seeing that $\alpha\gamma$-propane- and $\alpha\epsilon$-pentane-disulphonyl chlorides, as we have shown, react normally with ammonia or aromatic bases,

yielding diamides, it seemed desirable to inquire further into the behaviour of ethanedisulphonyl chloride with aromatic bases.

It was assumed, to begin with, that as the substance III was formed at the ordinary temperature it was probably the first product, which, by losing aniline hydrochloride, passed into I or II; but this view was negatived by the observation that neither compound could be readily converted into the other, both being comparatively stable. The following experiments were made :

(*a*) Compound III was heated in a dry tube; hydrogen chloride was evolved, but no aniline hydrochloride was formed.

(*b*) On heating compound III with water, the same result was obtained.

(*c*) Compound I was warmed with aniline; but the original substance was extracted unchanged.

(*d*) Aniline hydrochloride and compound I were ground up together and heated. Again no trace of compound III was obtained.

Autenrieth and Rudolph (*loc. cit.*), from the fact that compound I can be prepared from β-chloroethane-α-sulphonyl chloride, $CH_2Cl\cdot CH_2\cdot SO_2Cl$, and aniline, regard the reaction as probably proceeding in three stages, as follows :

$$1.\ \begin{matrix} CH_2\cdot SO_2Cl \\ | \\ CH_2\cdot SO_2Cl \end{matrix} + 2C_6H_5\cdot NH_2 = \begin{matrix} CH_2\cdot SO_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + C_6H_5\cdot NH_2,HCl.$$

$$2.\ \begin{matrix} CH_2\cdot SO_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} = \begin{matrix} CH_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + SO_2.$$

$$3.\ \begin{matrix} CH_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + C_6H_5\cdot NH_2 = \begin{matrix} CH_2 \\ \| \\ CH\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + C_6H_5\cdot NH_2,HCl.$$

In the same way, a fourth molecule of aniline might effect the following change, forming compound III.

$$4.\ \begin{matrix} CH_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + 2C_6H_5\cdot NH_2 = \begin{matrix} CH_2\cdot NH\cdot C_6H_5 \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{matrix} + C_6H_5\cdot NH_2,HCl.$$

We have attempted to follow the various stages in the process by successive additions of aniline in molecular proportions to ethanedisulphonyl chloride in ether solution, cooled in a freezing mixture.

On addition of two molecular proportions of aniline, a precipitate of aniline hydrochloride was thrown down mixed with an oily substance smelling strongly of mustard, which gradually decomposed emitting sulphur dioxide, the mustard smell disappearing at the same time. The reaction being supposed to take place in accordance with the above equation 1, the filtrate should contain no unchanged sulphonyl chloride. This proved to be the case. The oil was extracted with acetone, reprecipitated with water, and heated with alcoholic potassium hydroxide. The potassium chloride was removed by filtration and the alcohol by evaporation. The alkaline solution which remained was extracted with ether, and on removing the ether compound I was obtained. Another portion of the oil extracted with acetone combined readily with aniline, forming compound III in accordance with equation 4, whilst the action of potassium hydroxide would give the product of equation 3.

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2\cdot SO_2\cdot NH\cdot C_6H_5 \end{array} + KOH = \begin{array}{l} CH_2 \\ \| \\ CH\cdot SO_2\cdot NH\cdot C_6H_5 \end{array} + KCl + H_2O.$$

In order to ascertain whether the open- or closed-chain structure (formula I or II) should be assigned to the monosulphonanilide, Autenrieth and Koburger (*loc. cit.*) were able to show that, although the compound cannot be reduced by sodium amalgam, both the monosulphonanilide and the corresponding *p*-phenetidide form additive compounds with one molecule of bromine. Moreover, Autenrieth and Rudolph (*loc. cit.*) prepared a methyl, benzyl, and acetyl derivative, substances which are not likely to be formed in the case of a ring structure having formula II.

We have obtained further evidence in favour of this formula from a study of ethylenesulphonic acid, which is formed when the disulphonyl chloride is boiled with water.

This acid, like the monosulphonanilide, cannot be reduced with sodium amalgam, although, on heating it in a sealed tube at 170° with hydriodic acid, ethanesulphonic acid is formed.

Moreover, hydrogen chloride, hydrogen bromide, and water readily combine with the acid, which is therefore unsaturated. The acid was converted into the acid chloride, which, on combining with aniline, yielded the monosulphonanilide, identical with that obtained from the disulphonyl chloride.

$$\begin{array}{l} CH_2 \\ \| \\ CH\cdot SO_3H \end{array} \xrightarrow{PCl_5} \begin{array}{l} CH_2 \\ \| \\ CH\cdot SO_2Cl \end{array} \xrightarrow{C_6H_5\cdot NH_2} \begin{array}{l} CH_2 \\ \| \\ CH\cdot SO_2\cdot NH\cdot C_6H_5 \end{array}.$$

This result, together with the evidence of Autenrieth and Rudolph, *leaves no doubt as to the unsaturated, open-chain structure of the* monosulphonanilide.

EXPERIMENTAL.

Preparation of the Alkylene Dibromide.

Ethylene, propylene, and butylene dibromides were prepared by passing the olefines through bromine, the latter being obtained by a modification of Newth's method introduced by Mr. H. Calam. This method consists in running a slow stream of the alcohol through a fine glass spiral dipping below the syrupy phosphoric acid, whereby the alcohol is vaporised before contact with the hot phosphoric acid. By this means a steady current of gas is obtained, any alcohol which may escape decomposition being condensed by the aid of a small condenser attached to a Woulfe bottle, before the gas passes into the bromine. The best temperatures for the generation of the olefines from the alcohols were found to be 195° for ethylene, 240° for propylene, and 265° for butylene. At the higher temperatures, the phosphoric acid gradually attacks the glass vessel.

The olefine was passed through a tube of liquid bromine until the latter was decolorised. The product was purified in the usual way and distilled (the propylene and butylene bromides under reduced pressure).

Pentamethylene dibromide was prepared by von Braun's method by the action of phosphorus pentabromide on benzoylpiperidine.

Preparation of the Aliphatic Disulphonates.

The dibromides were in each case boiled with a saturated solution of sodium sulphite (2 mols.) until the lower oily layer had disappeared. On concentrating the solutions, the disulphonates crystallised, and by recrystallisation were readily obtained in a pure state. Propylene and butylene dibromides were decomposed during boiling, yielding the original olefine and sodium sulphate. Ammonium propanedisulphonate was, however, obtained by boiling the dibromide with a large excess of ammonium sulphite according to Monari's method (*Ber.*, 1885, **18**, 1345). The analyses of the anhydrous materials are as follows :

Sodium disulphonate.	Na per cent.		S per cent.		Water of crystallisation (mols.).
	Found.	Calculated.	Found.	Calculated.	
Ethane-	19·64	19·66	27·30	27·35	2
αβ-Propane-	—	—	27·10	26·90	—
αγ-Propane-	18·62	18·55	25·50	25·80	4·5
αε-Pentane-	16·90	16·69	23·50	23·20	5

Preparation of the Aliphatic Disulphonyl Chlorides.

The aliphatic disulphonyl chlorides were prepared by heating the disulphonates, carefully dried at 120° and finely powdered, with phosphorus pentachloride (2 mols.). When the mass had liquefied and no more hydrogen chloride was evolved, the phosphoryl chloride was either distilled off in a vacuum and the residue ground with ice-water and extracted with ether, or the oxychloride was removed on the water-bath and the residue ground with ice-water as before. The chlorides were crystallised from ether, chloroform, or benzene, and formed colourless, foliated crystals, the melting point and analytical data being as follows:

Disulphonyl chloride.	M. p.	Cl per cent. Found.	Cl per cent. Calculated.
Ethane-	91°	31·1	31·3
αβ-Propane-	48	29·2	29·46
αγ-Propane	45	29·3	29·40
αε-Pentane-	66	26·1	26·30

Action of Ammonia on the Aliphatic Disulphonyl Chlorides.

Ethylenesulphonamide.—Dry ammonia was led into a dry ether solution of the disulphonyl chloride. A white precipitate formed and nothing remained in the solution. The precipitate consisted of ammonium chloride and sulphite, a little ammonium ethanedisulphonate, and the sulphonamide. By careful evaporation of the dilute alcoholic solution most of the ammonium salts separated, and after removal and on further evaporation a sticky mass was obtained. This was dissolved in water, the remaining halogen removed with silver carbonate, and the mixture filtered and evaporated. It was again dissolved in a little water and reprecipitated with a large quantity of alcohol. After several repetitions of the process and on allowing the solution to evaporate slowly in a vacuum desiccator, a product, consisting of slender needles, was obtained which melted at 87°. The percentage of nitrogen (see below) corresponds with $C_2H_5O_2NS$, or ethylenemonosulphonamide, $CH_2{:}CH{\cdot}SO_2{\cdot}NH_2$.

αγ-Propane- and αε-Pentane-disulphonamides.—When treated with dry ammonia in ether solution, as described above, the disulphonyl chloride gave normal disulphonamides. The precipitate which formed was extracted with boiling acetone, and on removing the acetone the product was recrystallised from water or alcohol. In both cases colourless, foliated crystals were obtained either by

dissolving in hot alcohol and adding chloroform or by crystallising from hot water.

Sulphonamide.	M. p.	N per cent. Found.	Calculated.
Ethylenemonosulphonamide ...	87°	13·3	13·08
$\alpha\gamma$-Propanedisulphonamide ...	169	14·05	13·86
$\alpha\epsilon$-Pentanedisulphonamide	131	12·30	12·18

Action of Aniline on the Aliphatic Disulphonyl Chlorides.

The equivalent of four molecules of aniline in ether solution was added to one molecule of the disulphonyl chloride, also dissolved in ether. Aniline hydrochloride was precipitated, whilst the ether retained the sulphonanilide. In the case of ethane- and propane-disulphonyl chlorides, sulphur dioxide was at the same time evolved, as observed by Autenrieth and Rudolph. In that of $\alpha\gamma$-propane- and $\alpha\epsilon$-pentane-disulphonyl chlorides formation of normal disulphonanilides occurs, but proceeds slowly. The reaction can be hastened by conducting it in boiling benzene. With ethane-disulphonyl chloride, ethylenesulphonanilide and anilinoethane-sulphonanilide are formed simultaneously, as already explained, and the two may be separated by shaking the ether solution (after filtering the aniline hydrochloride) with dilute hydrochloric acid, which dissolves only the anilino-sulphonanilide.

Ethylenesulphonanilide crystallises from alcohol in colourless, foliated crystals, m. p. 69° (Autenrieth and Rudolph give 68°). The acetyl derivative was prepared by heating the sulphonanilide with excess of acetic anhydride, as described by Autenrieth and Rudolph. It crystallises from alcohol in needles, m. p. 99° (Autenrieth and Rudolph give 100°). According to the analysis its formula is $CH_2{:}CH{\cdot}SO_2{\cdot}N(C_2H_3O){\cdot}C_6H_5$ (Found : N = 6·4. Calc., N = 6·2 per cent.). The sulphonbenzylanilide, $CH_2{:}CH{\cdot}SO_2{\cdot}N(C_7H_7){\cdot}C_6H_5$, was also prepared by the method given by Autenrieth and Rudolph by way of confirmation, and was found to melt at 88° (Autenrieth and Rudolph give 87°) (Found : N = 5·3. Calc., N = 5·1 per cent.). Autenrieth and Rudolph obtained the methyl derivative by the action of methylaniline on the disulphonyl chloride and also by methylating ethylenesulphonanilide with methyl iodide in presence of sodium ethoxide. We obtained the same compound by using methyl sulphate in an alkaline solution of the sulphonanilide; it melted at 78° (Autenrieth and Rudolph give 77°) (Found : N = 7·2. Calc., N = 7·1 per cent.).

Propanedisulphonyl chloride, like the ethane derivative, gives an unsaturated monosulphonanilide, $CH_3{\cdot}CH{:}CH{\cdot}SO_2{\cdot}NH{\cdot}C_6H_5$. All the sulphonanilides can be crystallised from alcohol and form

colourless, foliated crystals. The reactions of the sulphonyl chlorides with *p*-toluidine are similar to those with aniline. With ethanedisulphonyl chloride a monosulphotoluidide is formed, which it is difficult to crystallise or purify, and a toluidinoethanesulphotoluidide hydrochloride, which crystallises in long, colourless needles. The following table gives the melting points and analyses:

Anilide.	M. p.	N per cent. Found.	N per cent. Calculated.
Ethylenesulphonanilide	69°	7·60	7·65
Anilinoethanesulphonanilide hydrochloride	171	8·40	8·50
αβ-Propanesulphonanilide	91	7·00	7·10
αγ-Propanedisulphonanilide	129	7·95	7·90
αε-Pentanedisulphonanilide	121	7·20	7·30
p-Toluidinoethanesulphotoluidide hydrochloride	165	N 11·07 Cl 14·10	11·26 14·30

The sulphonanilides can be readily methylated by Ullmann's method with methyl sulphate in alkaline solution. The following table gives the melting points of the methyl derivatives of the αγ-propane- and αε-pentane-disulphonanilides, together with the unmethylated compounds.

	M. p. Unmethylated.	M. p. Methylated.
αγ-Propanedisulphonanilide	129°	151°
αε-Pentanedisulphonanilide	121	100

Action of Phenylhydrazine on the Aliphatic Disulphonyl Chlorides.

Phenylhydrazinoethanesulphonylphenylhydrazide Hydrochloride.—The equivalent of four molecules of phenylhydrazine in ether was mixed with one molecule of ethylenesulphonyl chloride. Phenylhydrazine hydrochloride was precipitated and at the same time sulphur dioxide was evolved. After filtration, the ether solution was extracted with dilute hydrochloric acid, which removed the main product; a small quantity of a red oil remained after evaporating the ether and was not further examined. The acid extract was evaporated in a vacuum desiccator over sulphuric acid and sodium hydroxide, and the dark residue was brought on to a filter and rapidly washed with acetic acid. The residue, freed from acetic acid, was crystallised from alcohol. The compound forms slender needles which melt with decomposition at 188°. The analysis corresponds with the formula $\begin{matrix} CH_2\cdot NH\cdot NH\cdot C_6H_5,HCl \\ CH_2\cdot SO_2\cdot NH\cdot NH\cdot C_6H_5 \end{matrix}$ (Found: N = 16·45. $C_{14}H_{19}N_4ClS$ requires N = 16·55 per cent.).

αγ-Propanedisulphonyldiphenylhydrazide.—The reaction was

carried out as above. A thick, white precipitate was thrown down, but no sulphur dioxide was evolved. The ether extract contained a very small quantity of a substance melting with decomposition at 135°. The original precipitate was extracted with boiling water, which dissolved the phenylhydrazine hydrochloride, leaving a portion insoluble in ether or water and sparingly soluble in alcohol. When crystallised from aqueous acetone, it separated in slender, colourless needles melting with decomposition at 177°. The analysis corresponds with the formula of a normal disulphonyldiphenylhydrazide, $CH_2(CH_2{\cdot}SO_2{\cdot}NH{\cdot}NH{\cdot}C_6H_5)_2$ (Found : N = 14·5. $C_{15}H_{20}N_4S_2$ requires N = 14·58 per cent.).

Action of Hydrazine on the Aliphatic Disulphonyl Chlorides.

αγ-Propanedisulphonyldihydrazide, $CH_2(CH_2{\cdot}SO_2{\cdot}NH{\cdot}NH_2)_2$, was obtained by heating together in absolute alcohol one molecule of the sulphonyl chloride and three molecules of hydrazine hydrate. A precipitate of the hydrazide and a little hydrazine hydrochloride separated, the bulk of the latter remaining in solution. The hydrazide was filtered and crystallised from alcohol with the addition of a few drops of water. It crystallised in long, colourless needles which melted with decomposition at 105° (Found : N = 24·35. $C_3H_{12}O_4N_4S_2$ requires N = 24·1 per cent.).

αε-Pentanedisulphonyldihydrazide,

$$NH_2{\cdot}NH{\cdot}SO_2{\cdot}CH_2{\cdot}[CH_2]_3{\cdot}CH_2{\cdot}SO_2{\cdot}NH{\cdot}NH_2,$$

was prepared as above and crystallised similarly in needles melting with decomposition at 115° (Found : N = 21·7. $C_5H_{16}O_4N_4S_2$ requires N = 21·5 per cent.).

THE ORGANIC CHEMICAL LABORATORIES,
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XIX.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part II. Intra-annular Tautomerism.*

By ERNEST HAROLD FARMER, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

As many well-known examples prove, the chemistry of condensed, and sometimes of supposedly simple, alicyclic ring compounds is frequently complicated by extraordinary transformations and

inter-relationships which it would be quite impossible for anyone to predict from an examination of the structural formulæ of the substances concerned. One might quote as instances any of the changes which connect the three series of compounds derived respectively from camphene, pinene, and bornylene, or the conversion of α-campholytic and α-campholenic acids into their isomerides, *iso*lauronolic and β-campholenic acids, and it is probable that many who have given consideration to these and similar changes have drawn the conclusion that there must be some important fundamental fact connected with the chemistry of alicyclic ring compounds which still awaits discovery.

Of the methods which have been used for the determination of the structures of alicyclic substances, not only in terpene and camphor chemistry, but also in connexion with the alkaloids, and, generally, wherever complex ring structures are met with, none, probably, has been so widely employed or so implicitly relied on as the process of subjecting the substance under examination to regulated oxidation by cold alkaline permanganate. This being the case, the establishment of an instance in which oxidation by cold alkaline permanganate definitely and inevitably points to an incorrect constitution for the substance oxidised is, to say the least, disturbing and calls for further investigation.

In Part I of this series (T., 1920, **117**, 1362) it was shown that dimethyl*dicyclo*pentanonedicarboxylic acid (I), which, by synthesis from a *cyclo*propane derivative, by oxidation (with ferricyanide) to caronic acid, and by the study of its simplest reactions, was proved to have the bridge-ring structure (I), on oxidation by means of cold alkaline permanganate behaved as though it had the unsaturated structure (II); it passed quickly and quantitatively into αα-dihydroxy-ββ-dimethylglutaric acid (III) and oxalic acid.

$$CMe_2<\begin{array}{l}C(CO_2H)\cdot CH\cdot CO_2H \\ CH \text{———} CO\end{array} \quad (I.)$$

$$\underset{(II.)}{CMe_2<\begin{array}{l}C(CO_2H){=}C\cdot CO_2H \\ CH_2 \text{———} CO\end{array}} \longrightarrow \underset{(III.)}{CMe_2<\begin{array}{l}C(OH)_2\cdot CO_2H \\ CH_2\cdot CO_2H\end{array}} + CO_2H\cdot CO_2H.$$

Had the substance been a natural product, or had it been originally obtained in any way other than by a direct and rational synthesis, no search would have been made for some less commonly employed oxidising agent, and, on the basis of its behaviour with permanganate, it would certainly have been set down to be an unsaturated derivative of the formula II; and it is highly improbable, moreover, that any of the known facts regarding its chemistry

would have aroused a suspicion that this conclusion was not well founded.

It seemed essential, therefore, to discover whether this was an isolated instance, or, if not, under what conditions the existence of such examples of chemical perjury might be suspected. Moreover, it seemed probable that a study of the matter might also do much towards dispersing the mystery which at present envelops the mechanism of those curious alicyclic transformations referred to above; that both problems would be found to be co-extensive in the sense that not only these transformations, but also the misleading oxidation reactions, might be traceable to the operation of some fundamental but hitherto unrecognised circumstance.

The view to which we have been led by a close study of a number of compounds of the *dicyclo*pentane series may be briefly stated in the following terms. In cyclic compounds there exists, either potentially or actually, a kind of tautomerism, analogous in some respects to the three-carbon tautomerism of the glutaconic acids, but, in addition, involving valency-exchange across the ring. It will be our object in the present and subsequent parts of this series of papers to show how the occurrence of this phenomenon, which, in future, we may refer to as "intra-annular" tautomerism, lies at the basis of, not only the remarkable changes of structure previously mentioned, but also those mutually contradictory decompositions in the bridged-ring series which are best interpreted by ascribing to each compound a dual set of properties. The phenomenon of intra-annular tautomerism reaches its culminating point in benzene and its derivatives.

At the outset of the investigation it appeared that an excellent illustration of a substance capable of exhibiting mutually irreconcilable decompositions was ready to hand in the dimethyl*dicyclo*pentanonecarboxylic acid (IV), the constitution of which rests on its synthesis from a *cyclo*propane derivative, its oxidation to caronic acid, and its intimate relationship with the acid I, from which it may be obtained in quantitative yield by heating to its melting point in dry naphthalene :

(I.) (IV.)

Now Perkin and Thorpe showed (T., 1901, 79, 729) that the acid IV passed on treatment with alkaline permanganate into αα-dihydroxy-ββ-dimethylglutaric acid (III), and it is true that both the *dicyclo*pentane acids (I and IV) can be converted almost quantitatively by cold alkaline permanganate into the same acid (III) with approxi-

mately equal ease. By all accepted rules of evidence, therefore, this reaction, in the case of the acid IV, would seem to point conclusively to the unsaturated constitution (V):

$$CMe_2<\begin{matrix}C(CO_2H){:}CH \\ CH_2\text{——}CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}C(OH)_2{\cdot}CO_2H \\ CH_2{\cdot}CO_2H\end{matrix} + CO_2.$$

(V.) (III.)

It may be stated at once that the experiments described in this paper point, we believe unquestionably, to this equation as representing the true manner of the oxidation; that the acid V is a tautomeric modification of the acid IV, which reacts as though it were the unsaturated isomeride in the presence of a suitable reagent for unsaturated compounds:

$$\text{(IV.)}\quad CMe_2<\begin{matrix}C(CO_2H){\cdot}CH[H] \\ CH\text{———}CO\end{matrix} \rightleftharpoons CMe_2<\begin{matrix}C(CO_2H){:}CH \\ CH[H]-CO\end{matrix}\quad \text{(V.)}$$

(Mobile hydrogen atom shown: [H])

However, it will be observed that an alternative explanation is possible. One might suppose, unlikely as such a reaction seems, that, under the influence of the cold permanganate, the elements of water (not two hydroxyl groups) are added to the molecule by fission of the bridge, and that complete disruption of the remaining ring occurs subsequently, in the sense of the following equation:

$$CMe_2<\begin{matrix}C(CO_2H){\cdot}CH_2 \\ CH\text{——}CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}C(OH)(CO_2H)\text{-}\text{-}CH_2 \\ CH_2\text{————}CO\end{matrix} \longrightarrow$$

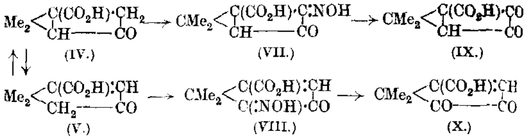
(IV.) (VI.)

$$CMe_2<\begin{matrix}C(OH)_2{\cdot}CO_2H \\ CH_2{\cdot}CO_2H\end{matrix} + CO_2.$$

(III.)

Such a scheme, the essential feature of which is the intermediate production of the hydroxy-acid (VI), might be adopted to explain, not only the oxidation by permanganate, but also a number of the reactions and decompositions described below, and in order to appreciate its inadequacy it is necessary to examine the evidence in some detail.

The original acid (IV or V), on treatment with nitrosyl chloride, yields a pale yellow oximino-derivative, which, on hydrolysis by means of hydrochloric acid in the presence of formaldehyde (compare Perkin, Roberts, and Robinson, T., 1912, **101**, 234), gives a diketonic acid, which might have formula IX or formula X, according to whether the original acid reacts in the form IV or the form V:

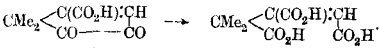


(IV.) (VII.) (IX.)

(V.) (VIII.) (X.)

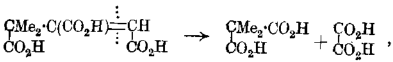
Now it has been conclusively proved that the oximino-compound has the constitution VIII and not VII, and that the diketonic acid has the structure X. The possibility of the formation of the oximino-compound VIII directly from the bridged acid IV will be referred to below.

In the first place, it should be noticed that the diketone was obtained in two forms, a more stable bluish-red form and a less stable orange modification. These appeared to be interconvertible in solution, but their stabilities at the ordinary temperature were sufficiently similar to enable them to be crystallised side by side; on the other hand, the orange form passed instantly into the red one on melting. Whether these two modifications are merely physical isomerides or whether they bear to one another some such relationship as is suggested by the diketone and peroxide formulæ for *ortho*-quinones is still in doubt, but, however this may be, there can be no question but that the two modifications are not position-isomerides having the respective formulæ IX and X; for in their chemical properties both forms are identical, and with cold dilute alkaline hydrogen peroxide both pass easily and quantitatively into dimethylaconitic acid (XI), a reaction which conclusively proves the structure X to be the correct one :



(X.) (XI.)

Dimethylaconitic acid does not appear to have been prepared previously, but it was readily characterised by oxidation by means of cold alkaline permanganate to dimethylmalonic acid and oxalic acid :



and by the formation, on treating with water at 180°, of dimethylitaconic acid (XII), which has already been prepared and characterised by Ssemenoff (*J. Russ. Phys. Chem. Soc.*, 1898, **23**, 490).

This reaction evidently involves the movement of a double bond so soon as the elimination of a carboxyl group renders this possible :

$$CMe_2(CO_2H)\cdot C(CO_2H){:}CH\cdot CO_2H \longrightarrow CHMe_2\cdot C(CO_2H){:}CH\cdot CO_2H \longrightarrow$$
$$CMe_2{:}C(CO_2H)\cdot CH_2\cdot CO_2H.$$
(XII.)

It should also be noticed that the diketonic acid, in agreement with its unsaturated formula (X), distils without eliminating its carboxyl group as carbon dioxide. This would certainly be most unlikely were the substance a β-ketonic acid having formula IX.

It will be observed that the diketonic acid (X) is quite incapable of change into any tautomeric modification having a bridged *cyclo*pentane nucleus. The diketonic acid is, in fact, a non-tautomeric derivative formed by the replacement of the potentially mobile hydrogen atom in the unsaturated form of the tautomeric parent substance.

If further evidence were required of the real existence of the unsaturated modification (V) of the original acid, it is to be found in the action of ferricyanide on this substance. We were not able definitely to identify all the oxidation products obtained by the action of this reagent owing to the difficulty of separating them from one another in the pure condition, but, nevertheless, succeeded in isolating, besides a small proportion of caronic acid derived directly from the bridged form (IV), a moderate quantity of dimethylaconitic acid (XI) evidently derived from the unsaturated form. For it is clear that if the hydroxy-acid VI were an intermediate product, fission of the ring would give rise to dimethylcitric acid (XIII), which would certainly not pass into dimethylaconitic acid under the experimental conditions employed :

$$CMe_2{<}\begin{matrix}C(OH)(CO_2H)\cdot CH_2\\ CH_2\text{———}CO\end{matrix} \dashrightarrow CMe_2{<}\begin{matrix}C(OH)(CO_2H)\cdot CH_2\\ CO_2H \qquad\quad CO_2H\end{matrix}.$$
(VI.) (XIII.)

Obviously, then, the formation of dimethylaconitic acid must occur by direct fission of the unsaturated modification of the acid,

$$\text{(V.)}\ CMe_2{<}\begin{matrix}C(CO_2H){:}CH\\ CH_2\text{—}CO\end{matrix} \longrightarrow CMe_2{<}\begin{matrix}C(CO_2H){:}CH\\ CO_2H \quad CO_2H\end{matrix}\ \text{(XI.)},$$

whilst the simultaneous production of caronic acid (XIV), which cannot but be derived from the bridged modification,

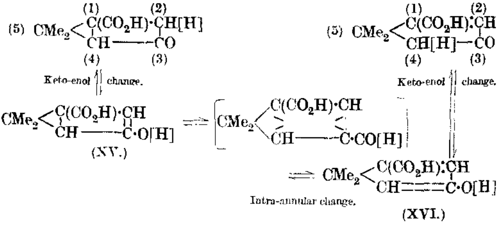
$$\text{(IV.)}\ CMe_2{<}\begin{matrix}C(CO_2H)\cdot CH_2\\ CH\text{———}CO\end{matrix} \longrightarrow CMe_2{<}\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix},\ \text{(XIV.)}$$

affords a remarkable example of the impossibility of interpreting

the reactions of these compounds on the basis of a single structural formula for each.

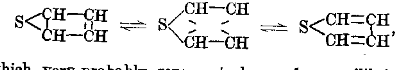
There can be little room for question, then, but that certain bridged acids of the *dicyclo*pentane series are, in some circumstances, capable of reacting as though they were unsaturated isomerides, and that the whole chemistry of these substances is built up of self-contradictory evidence of a type which, ever since Baeyer's classical study of the example afforded by isatin, has been of basic importance in the development of the conception of tautomerism.

In our instances, the tautomerism has an intra-annular character and it is of the utmost importance to examine carefully the conditions which underlie the intra-annular interchanges. It is clear that the transformation of the acid IV, for example, into the unsaturated form, V, must involve the passage of a hydrogen atom across the *cyclo*butane ring from position 2 to position 4. The most natural assumption that can be made as to the mechanism of this change would seem to be that the mobile hydrogen atom passes by way of the ketonic oxygen atom (position 3), which becomes a kind of stepping-stone. The actual intra-annular change, therefore, occurs between the two enolic forms,



(XV.) (XVI.)

which are obviously mere "valency-isomerides," related to one another, and to the hypothetical intermediate phase shown in square brackets, after the manner of the various formulæ which have at different times been proposed for thiophen,

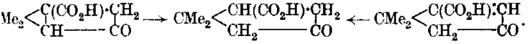


and which, very probably, represent phases of an equilibrium.

The adoption of this explanation not only greatly simplifies the character of the intra-annular interchanges which have to be assumed, but also offers a reasonable explanation of the fact that

in the case of the dibasic acid (I) the bridged form appears to be relatively more permanent than in the case of the monobasic acid (IV). That this is so is shown by several circumstances, for instance, by the smaller yield of caronic acid obtained from the monocarboxylic acid, and again by the fact that, as preliminary experiments have indicated, the dicarboxylic acid does not yield appreciable quantities of an oximino-derivative when treated with nitrosyl chloride under conditions in which the oximino-compound of the monobasic acid is readily obtained : according to the evidence given above, the oximino-compound is derived from the unsaturated modification. Clearly the attachment of a carboxyl group at position 2 would have the effect of stabilising the bridged enolic phase (XV), since the compound is now a substituted acetoacetic acid, and by thus reducing the permanence of the unsaturated enolic phase (XVI) would favour the reactions of the bridged modification.

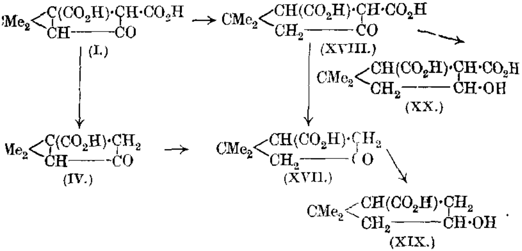
In this connexion it is worth while considering the behaviour of the acids on reduction by sodium amalgam. Obviously either the bridged acid (IV) or its unsaturated form (V) would yield the same dihydro-derivative (XVII), the production of which, therefore, is no indication of the manner in which it is formed :



(IV.) (XVII.) (V.)

Now, in a paper on the stability of bridged *spiro*-compounds (Ingold and Thorpe, T., 1919, **115**, 320), a quantitative study of the velocity of reduction of the monocarboxylic acid (IV or V) to the dihydro-acid (XVII) is recorded, and the velocity is found to be of the order of magnitude to be expected from considerations arising directly out of the strained-valency hypothesis which forms the basis of that paper, and founded on the assumption that it is the *bridged* form (IV) which undergoes reduction. Since the same would not be true were the unsaturated modification responsible for the production of the acid XVII, we may take this result to indicate that the main process occurring during the reduction is the fission of the bridge-bond in the acid IV. It follows that the dicarboxylic acid (I) should undergo reduction considerably more readily on account of its more permanent bridged phase, and this is actually found to be the case. The dibasic dihydro-acid (XVIII), which is formed more than twenty times as rapidly as its analogue (XVII), is only stable in the form of its salts; these, on treatment with mineral acids, yield carbon dioxide and the monobasic reduction product (XVII). The existence of the acid XVIII in alkaline

solution is proved by the fact that on prolonged reduction it is converted, by addition of hydrogen to the ketone group, into the hydroxy-acid (XX), which is quite stable and exhibits no tendency to pass, by loss of a carboxyl group as carbon dioxide, into the ultimate reduction product (XIX) of the monocarboxylic acid :



On page 134 an analogy was drawn between the acids of the *dicyclo*pentane series and those remarkably stable, five-membered ring systems of which thiophen and furan are typical instanees. In view of this analogy, and, indeed, the whole character of these acids as products derived from an intra-annular tautomeric system, similar in certain respects to the benzene nucleus, it seemed remarkable that Toivonen (*Annalen*, 1919, **419**, 212) should have obtained from the monocarboxylic acid (IV) and bromine a dibromo-additive product, the formation of which he regarded as proof that he acid had a simple *cyclo*pentene structure. Unfortunately, however, an estimation of the bromine content only is insufficient in this case to distinguish between addition and substitution, and Toivonen did not make a complete analysis of his dibromo-derivative. Had he done so, he would have at once discovered that the product was formed by substitution and not by addition, and that its empirical formula contained two atoms of hydrogen less than the number he assigned. Toivonen does not record his yield, but states that he used somewhat more than two atoms of bromine for one molecule of the monocarboxylic acid, and that hydrogen bromide was evolved towards the end of the process. We have carefully examined the products obtained by the action of varying quantities of bromine on the acid under the exact conditions employed by Toivonen, which are in every way excellent, and we have found that in order to obtain a good yield of the dibromo-acid (80 per cent. of the theoretical of pure, twice recrystallised material) it is necessary

to employ four and not two atoms of bromine, and that when two atoms of bromine are used the product consists almost entirely of a monobromo-derivative which Toivonen failed to isolate; further, although in all cases hydrogen bromide is evolved only after the reaction has proceeded a certain distance and the solvent employed has become saturated with the gas, its generation in solution takes place from the commencement. It seems impossible, therefore, to entertain the slightest doubt but that we are dealing, not with addition, but with a series of consecutive substitution reactions in agreement with the analogies to which we have been led.

Having established these points, it seemed that the whole matter was sufficiently curious and interesting to warrant a more extended examination, and, to this end, the chloro-derivatives (which were chosen in place of the bromine compounds in order that additive products, if formed, could be more easily identified by analysis owing to the lower atomic weight of chlorine) of the mono- and di-carboxylic acids (IV and I) were investigated, with results which clearly show the manner in which substitution may take place in such an intra-annular tautomeric system.

Chlorination of the monocarboxylic acid (IV) appears to take place more easily than bromination. In chloroform solutions at the ordinary temperature, with a moderate excess of chlorine, the product is a mixture, of which the di- and tri-chloro-substitution products of the original acid are the principal constituents, the former predominating. Several attempts were made, by arresting the process at an earlier stage, to isolate a monochloro-compound analogous to the monobromo-derivative described above. However, the solubilities in many organic solvents and in water of the mono-chloro-compound (see below) and of the dichloro-compound are very similar to one another and to that of the original monocarboxylic acid, so that a mixture of all three substances is very difficult if not impossible to separate into its constituents by fractional crystallisation. Owing to this, the monochloro-derivative could not be obtained in the pure condition by this method, but there can be no question but that the di- and tri-chloro-compounds are substitution and not addition products, for not only analysis, but also a study of the decompositions of the substances furnished conclusive evidence. The monochloro-compound is most readily prepared by treating the dicarboxylic acid (I) with the theoretical amount of chlorine in chloroform suspension, a carboxyl group being eliminated as carbon dioxide during the process. With an excess of chlorine, the main product is the trichloro-derivative, whilst, if an intermediate amount be employed, a mixture is obtained from which it is possible to separate the mono- and tri-chloro-compounds and an

intermediate fraction which very probably contained the dichloro-derivative. These mono-, di-, and tri-chloro-compounds have respectively the following formulæ,

$$CMe_2<\begin{matrix}C(CO_2H)\cdot CHCl\\ CH\text{———}CO\end{matrix}\qquad CMe_2<\begin{matrix}C(CO_2H)\cdot CHCl\\ CCl\text{———}CO\end{matrix}$$

(XXI.) (XXII.)

$$CMe_2<\begin{matrix}C(CO_2H)\cdot CCl_2\\ CCl\text{———}CO\end{matrix},$$

(XXIII.)

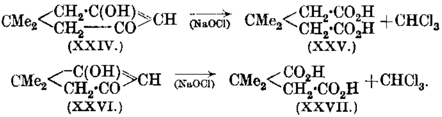
as has been proved by a study of their products of hydrolysis. The mono- and di-bromo-derivatives doubtless have formulæ analogous to those of the mono- and di-chloro-compounds (XXI and XXII).

The type of decomposition which these substances undergo on treatment with dilute alkalis is similar in all cases. It may be illustrated by reference to the monobromo-compound (XXVIII), which reacts according to the following scheme :

$$C_8H_9O_3Br + NaOH = C_7H_{10}O_2 + NaBr + CO_2.$$

Although the carboxyl group present in the original substance has evidently been eliminated as carbon dioxide, the product, $C_7H_{10}O_2$, which is beautifully crystalline and separates from water in large, well-defined prisms, is strongly acidic : it causes a vigorous evolution of carbon dioxide from sodium hydrogen carbonate and titrates as a monobasic acid in the presence of phenolphthalein. For some time the nature of this acid remained obscure, but ultimately it was discovered that it gave an intense red coloration with ferric chloride, an observation which rendered it immediately evident that the substance was the enolic form (dimethyl*cyclo*pentenolone, XXVI) of dimethyl*cyclo*pentanedione, and therefore the lower ring-homologue of dimethyldihydroresorcinol (XXIV), which, as is well known, titrates as a monobasic acid, gives a strong ferric chloride reaction, and shows a remarkable tendency to separate from water in large and well-defined crystals. Fortunately, it is an easy matter to show that the acid $C_7H_{10}O_2$ really has the formula XXVI, for Vorländer has shown (*Ber.*, 1899, **32**, 1878) that dimethyldihydroresorcinol may be oxidised almost quantitatively by means of sodium hypochlorite to ββ-dimethylglutaric acid (XXV) and chloroform. Consequently, the *cyclo*pentane analogue (XXVI) should yield *as*-dimethylsuccinic acid (XXVII) and chloroform when treated with alkaline hypochlorite under similar conditions. Actually the acid $C_7H_{10}O_2$ may be converted by means of hypochlorite into

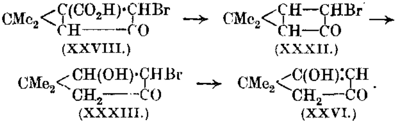
as-dimethylsuccinic acid and chloroform in almost quantitative yield:



(XXIV.) (XXV.) (XXVI.) (XXVII.)

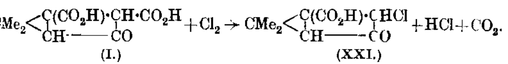
The extremely close analogy between the acid XXVI and dimethyldihydroresorcinol is yet more strikingly emphasised by the behaviour of the chloro-derivatives described below.

The mechanism of the formation of the acid XXVI from the bromo-compound is clear: the carboxyl group has been eliminated, the elements of water have been added at the bridge-bond, and hydrogen bromide has been eliminated:



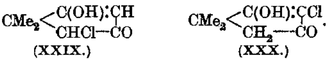
(XXVIII.) (XXXII.) (XXXIII.) (XXVI.)

The correctness of the corresponding formula (XXI) for the monochloro-derivative is confirmed by the fact that it is formed from the dicarboxylic acid (I) with the elimination of a carboxyl group from the position into which the chlorine atom enters:



(I.) (XXI.)

When the dichloro-compound is treated with dilute alkalis, a decomposition takes place which is strictly analogous to that of the monobromo-derivative. The product is an acid, $C_7H_9O_2Cl$, which titrates well and gives a colour with ferric chloride. It is evidently a monochloro-derivative of dimethyl*cyclo*pentenolone (XXVI), and might, *a priori*, have either of the following formulæ:



(XXIX.) (XXX.)

Fortunately, however, it is an easy matter to distinguish between these formulæ both by synthesis and by oxidation; for the product of directly monochlorinating dimethyl*cyclo*pentenolone can only

have the formula XXX, whilst on oxidation by alkaline hypo chlorite an acid of the structure XXIX should give chloro-*as* dimethylsuccinic acid, and one of the formula XXX should giv dimethylsuccinic acid itself. Actually the monochlorination produc of dimethyl*cyclo*pentenolone is isomeric, and not identical, with th substance obtained by the action of sodium hydroxide on th dichloro-derivative. The latter must therefore be represented b formula XXII, and its product of alkaline hydrolysis by the formul XXIX. The substance XXIX, on oxidation by hypochlorite passes, as it should, into the chloro-derivative XXXI of *as*-di methylsuccinic acid and chloroform :

$$CMe_2<\begin{matrix}C(OH):CH\\ CHCl-CO\end{matrix} \xrightarrow{NaOCl} CMe_2<\begin{matrix}CO_2H\\ CHCl\cdot CO_2H\end{matrix} + CHCl_3.$$

(XXIX.) (XXXI.)

The formation of the chloro-acid XXIX, in contrast to that o its isomeride, XXX (see below), therefore takes place in the follow ing stages :

$$CMe_2<\begin{matrix}C(CO_2H)\cdot CHCl\\ CCl----CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}CH-CHCl\\ CCl--CO\end{matrix} \longrightarrow$$

(XXII.) (XXXIV.)

$$CMe_2<\begin{matrix}CH(OH)-CHCl\\ CHCl---CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}C(OH):CH\\ CHCl-CO\end{matrix}.$$

(XXXV.) (XXIX.)

Alkaline hydrolysis of the trichloro-acid (XXIII) pursues a interesting course. In the cases just dealt with, it will be observe that the first two steps (leading to the formation of the compound XXXII and XXXIII in one example and XXXIV and XXXV i the other) are completely analogous, and it is therefore to be ex pected that the trichloro-compound will behave in a similar manne and give rise to the substances XXXVI and XXXVII. The com pound XXXVII may now split off hydrogen chloride in two ways giving rise either to the acid XXXVIII, which is a dichloro-substitu tion product of the parent 1 : 3-diketone, or to the compound XXXIX :

$$CMe_2<\begin{matrix}C(CO_2H)\cdot CCl_2\\ CCl----CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}CH-CCl_2\\ CCl-CO\end{matrix} \longrightarrow$$

(XXIII.) (XXXVI.)

$$CMe_2<\begin{matrix}CH(OH)-CCl_2\\ CHCl---CO\end{matrix} \longrightarrow CMe_2<\begin{matrix}C(OH)=CCl\\ CHCl--CO\end{matrix} \quad \text{or}$$

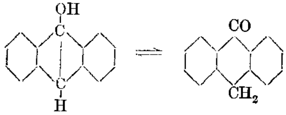
(XXXVII.) (XXXVIII.)

$$CMe_2<\begin{matrix}C(OH)-CCl_2\\ CH---CO\end{matrix}.$$

(XXXIX.)

Now, it is obvious that these two substances are very easily distinguished; for, whilst the first is a stable monobasic acid, the second is the tautomeric form of dichlorodimethyl*cyclo*pentadione (XL), to which it is related just as anthranol is to anthrone :

$$\text{(XXXIX.)}\quad CMe_2<\begin{matrix}C(OH)\cdot CCl_2\\ |\qquad\quad |\\ CH\text{——}CO\end{matrix} \rightleftharpoons CMe_2<\begin{matrix}CO\text{—}CCl_2\\ |\qquad |\\ CH_2\text{—}CO\end{matrix}\quad\text{(XL.)}$$

(*Anthranol*)  (*Anthrone*).

However, as Norris and Thorpe have recently shown (T., 1921, **119**, 1202), *gem*-dihalogen derivatives of dihydroresorcinol are spontaneously reduced in alkaline solution to the monohalogen compounds, hypochlorous acid or hypobromous acid being eliminated :

$$CMe_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CBr_2+H_2O \xrightarrow[(NaOH)]{} CMe_2<\begin{matrix}CH_2\cdot C(OH)\\ CH_2\cdot CO\text{——}\end{matrix}>CBr+HOBr.$$

Consequently, it is to be expected that the dichloro-derivative (XL) of the five-carbon ring analogue of dimethyldihydroresorcinol would behave similarly, and, in the presence of dilute alkalis, would pass into the monochloro-compound (XXX) :

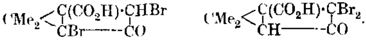
$$\underset{\text{(XL.)}}{CMe_2<\begin{matrix}CO\text{——}CCl_2\\ |\qquad |\\ CH_2\text{—}CO\end{matrix}}+H_2O \xrightarrow[(NaOH)]{} \underset{\text{(XXX.)}}{CMe_2<\begin{matrix}C(OH){:}CCl\\ |\qquad |\\ CH_2\text{——}CO\end{matrix}}+HOCl.$$

Actually this is what occurs. The monochloro-acid (XXX) was readily identified by synthesising it from the parent substance (XXVI) by direct chlorination, and by the fact that it differed markedly from the only other possible isomeride (XXIX), the constitution of which had been definitely established (above).

These reactions clearly prove that the original trichloro-acid (XXIII) has the constitution assigned to it, for the alternative formula (XLI) requires that the product of hydrolysis should be either XLII (tautomeric with XXXVIII), which it is not, or XLIII, which would not undergo spontaneous reduction with alkalis, and, if it did, could yield only the monochloro-acid (XXIX) and not the isomeride (XXX) actually obtained :

$$\underset{\text{(XLI.)}}{CMe_2<\begin{matrix}C(CO_2H){:}CCl\\ |\qquad |\\ CCl_2\text{——}CO\end{matrix}} \longrightarrow \underset{\text{(XLII.)}}{CMe_2<\begin{matrix}C(OH)\text{—}CHCl\\ |\qquad |\\ CCl\text{——}CO\end{matrix}}\ \textit{or}\ \underset{\text{(XLIII.)}}{CMe_2<\begin{matrix}C(OH){=}CH\\ |\qquad |\\ CCl_2\text{——}CO\end{matrix}}.$$

The dibromo-substitution product of the original monocarboxylic acid has not yet been investigated in detail, but it is exceedingly probable that its formula is XLIV, although the alternative formula XLV must not be lost sight of in the meantime :

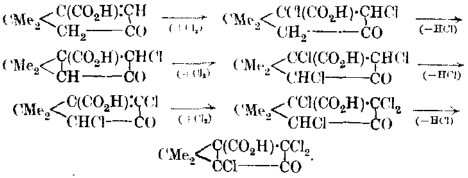


(XLIV.) (XLV.)

From the preceding discussion it will immediately be plain that although the mono-, di-, and tri-chloro-derivatives of the original monobasic acid were for convenience represented by the three bridged formulæ (XXI, XXII, and XXIII), the first two of these substances might equally correctly be expressed by the double-bonded formulæ XLVI and XLVII :

(XLVI.) (XLVII.)

Now, if one adopts the generally accepted views relating to the mechanism whereby substitution occurs in tautomeric systems, it is possible to express the production of these chloro-acids in the following way :



It will be observed that this scheme, which consists merely in alternately adding two atoms of chlorine and eliminating hydrogen chloride, leads to orientations for the successive substitution products in complete accord with the facts. It is equally true, although perhaps less obvious, that in order to obtain this result it is absolutely essential to utilise both the bridged and the unsaturated forms of the tautomeric substances involved; the orientation of the halogen compounds and their decompositions with alkalis therefore supply remarkably clear and convincing evidence for the view that the whole chemistry of these substances can find an adequate basis only in a dynamic conception of the constitution of the cyclic system which is their common nucleus.

It is probably the bridged forms, however, which, in every case, *are responsible for the hydrolytic decompositions brought about* by dilute alkalis. This is abundantly clear from what precedes, and it is for this reason that the non-tautomeric substance (XXIII) and the two tautomeric substances (XXI and XXII) react analogously.

The importance of the non-tautomeric trichloro-derivative (XXIII) in connexion with the evidence for tautomerism is very considerable, and is similar in nature to the importance of the *O*- and *N*-methyl ethers of isatin in connexion with the tautomerism of that substance. For by successive substitution by chlorine the potentially mobile hydrogen atom has at length been displaced, leaving a definitely non-tautomeric derivative of the bridged modification of the tautomeric parent-substance. The trichloro-acid, therefore, is the counterpart of the coloured diketonic acid (X), which is an equally definite non-tautomeric derivative of the unsaturated modification of the same tautomeric parent.

The formation of these non-tautomeric compounds by the substitution of appropriate groups for hydrogen in each of the individuals composing the original tautomeric system, taken together with the action of oxidising agents on the parent acids and the formation of oxidation products derived from both modifications, constitutes the evidence so far adduced for the phenomenon of *intra-annular tautomerism, and the proof of the structures of the* two individuals involved. The table on p. 144 summarises the position.

From the necessity for a dynamic conception, it follows that no certain conclusions can be drawn from the reactions of any of this series of compounds as to which formula expresses the constitution of the solid substance. Thns the original monocarboxylic acid (IV or V) has been isolated in one modification only, and it is impossible to tell whether the solid substance possesses the bridged formula (IV) or the double-bonded formula (V), since in solution it may react in either form. We have attempted, however, to obtain information on this point by preparing a bromo-acid (XLVIII), which, under carefully controlled conditions, might conceivably

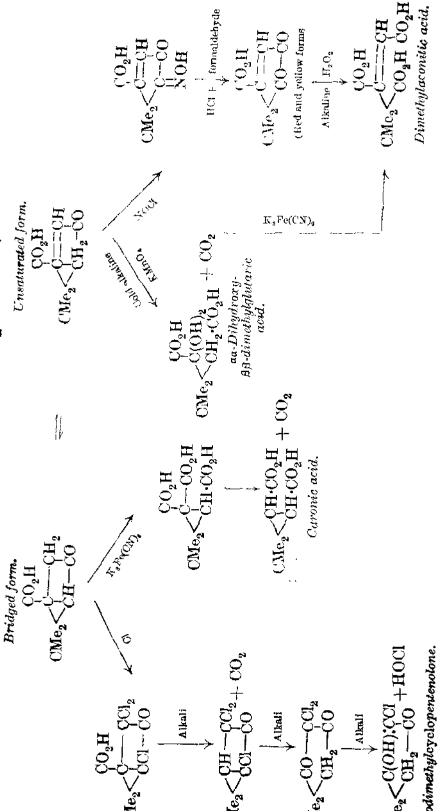
$$CMe_2{<}\begin{array}{l}CBr(CO_2H)\cdot CH_2\\ CH_2\text{———————}CO\end{array} \qquad CMe_2{<}\begin{array}{l}CH(CO_2H)\cdot CHBr\\ CH_2\text{—————}CO\end{array}$$

(XLVIII.) (XLIX.)

lose hydrogen bromide in such a manner as to give rise to the unknown form (whichever it be) of the original monobasic acid. The bromo-acid (XLVIII) was to be obtained by brominating the *cyclo*pentane acid (XVII), but, unfortunately, the monobromination

TABLE.

(Proof of the Structures of the Two Individuals.)



product was a mixture of two isomeric monobromo-acids, neither of which appeared to possess any tendency to pass, by elimination of hydrogen bromide, either into the expected monocarboxylic acid or into any other recognisable product. It seems probable that these two bromo-acids are *cis*- and *trans*-isomerides having the constitution XLIX, but their products of hydrolysis and of oxidation were intractable syrups the nature of which could not be ascertained.

Finally, it is necessary to mention a curious point which has arisen in connexion with chlorodimethylsuccinic acid (XXXI) referred to on p. 140. This substance, when crystallised from concentrated hydrochloric acid, does not separate in the free state but in the form of its anhydride, which was at first assumed to have the formula (L). The fact that it causes an effervescence with sodium hydrogen carbonate was explained by assuming that the dilute alkali immediately broke the anhydride ring, liberating the free dibasic acid. Further investigation showed, however, that a solution of the anhydride in water titrated, not as a dibasic acid, but as a monobasic acid, and, moreover, that it gave a pronounced crimson coloration with ferric chloride. These results prove that the substance is not a true anhydride but a "hydroxy-anhydride" (LI), similar in certain respects to glutaconic hydroxy-anhydride

$$\begin{matrix} CMe_2\cdot CO \\ CHCl\cdot CO \end{matrix}\!\!>\!O \qquad \begin{matrix} CMe_2\text{—}CO \\ CCl{:}C(OH) \end{matrix}\!\!>\!O \qquad CH\!<\!\begin{matrix} CH\text{——}CO \\ CH{:}C(OH) \end{matrix}\!\!>\!O$$

(L.) (LI.) (LII.)

(LII), which also titrates as a monobasic acid and gives a coloration with ferric chloride. So far as we are aware, however, chlorodimethylsuccinic acid is the first example of a *saturated* dibasic acid which gives rise to a hydroxy-anhydride on dehydration.

It is proposed to deal in future communications with the suppression of tautomerism by substitution and its manifestation in other cyclic systems, for instance, in compounds of the terpene and camphor series.

EXPERIMENTAL.*

(A) *Preparation of* 5 : 5-*Dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (IV *or* V) *from* 5 : 5-*Dimethyl*dicyclo*pentan*-3-*one*-1 : 2-*dicarboxylic Acid* (I *or* II).

When the dicarboxylic acid is heated above its melting point without the addition of a solvent, a considerable amount of charring takes place, and although large amounts of carbon dioxide are

* Substances showing intra-annular tautomerism are designated by the names of their bridged modifications.

evolved, the yield of monocarboxylic acid is poor. If, however, th dibasic acid is heated in dry naphthalene, the elimination of carbo: dioxide proceeds smoothly and the yield of monobasic acid is almos quantitative.

One gram of the dibasic acid was heated with dry naphthalen (5 grams) for six hours at 200—210°. The product was triturate with aqueous sodium carbonate solution, from which the monobasi acid (m. p. 180°) was extracted by means of ether after acidificatio by hydrochloric acid.

(B) *Oxidation of 5 : 5-Dimethyl*dicyclo*pentan-3-one-1-carboxylic Acid (IV or V) by Ferricyanide : Formation of* trans-*Caronic Acid (XIV), αα-Dimethylaconitic Acid (XI), and other Substances.*

(*a*) The monobasic acid (2·6 grams) was dissolved in a solution of potassium carbonate (2·34 grams) in water (20 c.c.), and treated at 40° with successive portions of a solution obtained by dissolving potassium ferricyanide (55·5 grams) and potassium carbonate (11·7 grams) in water. The total quantity of ferricyanide added during a period of five days corresponded with three atoms of available oxygen. The solution was cooled, acidified by means of hydrochloric acid, and extracted exhaustively with ether; the solid residue, which resisted all attempts to separate it into its constituents by fractional crystallisation, was dissolved in an excess of ammonia and the solution evaporated. The mixture of ammonium salts, although fully crystalline when dry, was very hygroscopic and had to be desiccated for several days before it was obtained in a condition satisfactory for separation by anhydrous solvents.

On triturating the mixture with warm absolute ethyl alcohol, a large amount passed into solution. The insoluble portion proved to be the ammonium salt of *trans*-caronic acid, which, when liberated in the usual way and crystallised once from water, had the correct melting point. It was identified by direct comparison with an authentic specimen, by a mixed-melting point determination, and by conversion into terebic acid.

The soluble ammonium salts were partly precipitated by adding ether. The precipitated portion yielded a mixture of acids, most of which was soluble in a few drops of water. On filtering, evaporating to dryness, and crystallising the residue several times from benzene, *anhydro-αα-dimethylaconitic acid* (see below) was obtained in a pure condition.

From the ammonium salt which remained in the ethereal solution an acid melting at about 170° was isolated, but it could

not be completely purified and its investigation was ultimately abandoned.

(*b*) The monobasic acid (4·5 grams) was dissolved in just sufficient potassium carbonate solution, and was treated with a solution prepared by dissolving potassium ferricyanide (38·4 grams, corresponding with two atoms of available oxygen) and potassium carbonate (16·1 grams) in 150 c.c. of water. The reaction mixture was heated on a steam-bath for eight hours, after which the evolution of carbon dioxide, due to gradual neutralisation of the carbonate, had ceased and the solution had turned yellow. The product was acidified by adding excess of hydrochloric acid, and extracted exhaustively by means of ether; the extract, on evaporation, yielded a white, crystalline solid containing admixed gummy material. The crude mixture was rubbed with a little cold water, and the undissolved portion, which consisted of unchanged monobasic acid, was collected. It weighed 1·4 grams after recrystallisation. The filtrate was evaporated to dryness, and the residue thoroughly dried in an evacuated desiccator and extracted several times with boiling benzene, from which *anhydro-αα-dimethylaconitic acid* separated on cooling (0·8 gram).

The portion which did not dissolve in benzene consisted of a brown gum containing a moderate amount of crystalline material, which was separated by taking advantage of its insolubility in acetone. By crystallisation from a mixture of methyl alcohol and benzene, it was obtained as a minutely crystalline powder which melted with decomposition at 154°. It was found to be insoluble in benzene, ether, or acetone, but very soluble in water or methyl alcohol. Unfortunately, the quantity was insufficient for analysis.

The characterisation of anhydro-αα-dimethylaconitic acid, which has not previously been prepared, is described on pp. 149, 150.

(C) *Action of Nitrosyl Chloride on* 5 : 5-*Dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (IV *or* V) *: Formation of* 4-*Oximino*-5 : 5-*dimethyl*-Δ^1-cyclo*penten*-3-*one*-1-*carboxylic Acid* (VIII), *and* 2 . 4-*Dichloro*-5 : 5-*dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (XXII).

The *dicyclo*pentane acid was suspended in dry chloroform and a current of dry nitrosyl chloride, derived from "chamber crystals," was passed through until the solvent was saturated, the temperature being maintained between −10° and −5°. The temperature was then allowed to rise gradually to that of the room during about four hours, after which the pale yellow, crystalline precipitate was collected and washed with chloroform.

On evaporation at room temperature, the filtrate deposited a crystalline solid which, after recrystallisation several times from chloroform and precipitation from aqueous solution by the addition of acetic acid, was obtained in the pure condition and was identified as the *dichloro-acid* described on p. 155.

4-Oximino-5 : 5-dimethyl-Δ^1-cyclo*penten-3-one-1-carboxylic Acid* (VIII).

The yellow precipitate consisted almost entirely of this oximino-acid, which was obtained in the pure condition by crystallisation from boiling water as stout, yellow prisms. The yield was 70—75 per cent. of the theoretical.

The acid separated from chloroform in minute, pale yellow, silky prisms. Although comparatively faintly coloured in the solid state and in solution, it gave intensely yellow solutions in aqueous alkalis. It darkened at 200—205° and rapidly decomposed at 205° (Found : C = 52·7; H = 5·1. $C_8H_9O_4N$ requires C = 52·5; H = 4·9 per cent.).

5 : 5-Dimethyl-Δ^1-cyclo*pentene-3 : 4-dione-1-carboxylic Acid* (X). (Red and orange modifications.)

The oximino-compound (5 grams) was warmed with 40 per cent. formaldehyde (20 grams) and excess of concentrated hydrochloric acid until, in the course of a few minutes, a clear and deeply orange-coloured solution was obtained. This was cooled and extracted repeatedly with ether. On evaporating the ether and residual formaldehyde, 4 grams of an intensely coloured, bluish-crimson solid remained, from which either of the two modifications could be obtained at will, according to the manner of recrystallising. The bluish-red form was best obtained by cooling a hot concentrated solution in benzene, and the orange modification by slow evaporation of a benzene solution saturated at room temperature.

Both forms crystallised in small, flattened prisms, the orange prisms usually being the larger. The red diketone melted at 145°; the orange form passed into the red form at about 117°. No factor determining the formation of the two modifications, other than rate of crystallisation, could be discovered, and their chemical identity appeared to be complete (Found: C = 57·5; H = 4·8. $C_8H_8O_4$ requires C = 57·2; H = 4·8 per cent.).

Formation of αα-Dimethylaconitic Acid (XI), *and its Anhydro-acid by Oxidation of the Red and Orange Modifications of the Diketone by means of Alkaline Hydrogen Peroxide.*

Two grams of either modification of the diketone were dissolved in a slight excess of aqueous sodium carbonate solution and treated with 1·7 per cent. hydrogen peroxide at the ordinary temperature. The colour of the solution rapidly became paler, and when, after a quantity of hydrogen peroxide equivalent to one atom of available oxygen had been added during the course of about five minutes, the solution was completely decolorised, it was rendered acid by means of hydrochloric acid and extracted repeatedly with ether. The colourless, crystalline solid which remained on evaporating the ether was found to be partly soluble and partly insoluble in boiling benzene.

αα-Dimethylaconitic Acid (XI).

The solid insoluble in boiling benzene was further purified by twice precipitating from solution in dry ether by adding light petroleum, and was thus obtained as a micro-crystalline acid, which melted at 138° with evolution of steam, giving a clear liquid. The acid, which was extremely soluble in water and moderately so in ether, was proved to have the constitution assigned to it by oxidation by alkaline permanganate, and by conversion into teraconic acid (below) (Found : C = 47·5; H = 5·0. $C_8H_{10}O_6$ requires C = 47·5; H = 5·0 per cent. By titration M = 202. Calc., M = 202). The same acid was obtained by hydration of the anhydro-acid (below.)

Anhydro-αα-dimethylaconitic Acid,

$$\begin{array}{l}CO\cdot O\cdot CO \\ CMe_2\cdot C{:}CH\cdot CO_2H\end{array} \quad or \quad \begin{array}{l}C(CO_2H){=}CH^* \\ CMe_2\cdot CO\cdot O\cdot CO\end{array}.$$

The acid which dissolved in boiling benzene was deposited on concentrating the solution and cooling as flattened, feathery needles, m. p. 148°. These, when freshly prepared, contained benzene of crystallisation, which was gradually given off in an evacuated desiccator, the crystals becoming opaque and readily friable (Found : C = 52·2; H = 4·5. $C_8H_8O_5$ requires C = 52·2; H = 4·4 per cent. On titration with 0·0264 *N*-barium hydroxide, the acid behaved as though it were tribasic : M = 186. Calc., M = 184).

* A third anhydro-acid is possible. However, it follows from the mode of formation of the dimethylaconitic acid that the modification isolated is that in which the two carboxyl groups adjacent to the unsaturated linking are in *trans*-positions relative to each other. Such an acid can give only two anhydro-acids without change of configuration.

The anhydro-acid was readily converted into the tribasic acid (above) by dissolving in hot alkalis, cooling, acidifying, and extracting by means of ether.

The anhydro-acid obtained by oxidising dimethyl*dicyclo*pentanonecarboxylic acid by means of alkaline ferricyanide (pp. 146, 147) was in every way identical (Found : C = 52·3 ; H = 4·5 per cent.) and yielded the same tribasic acid.

Oxidation of αα-Dimethylaconitic Acid by means of Cold Alkaline Permanganate : Formation of Dimethylmalonic Acid and Oxalic Acid.

The acid (0·5 gram) was dissolved in a slight excess of aqueous sodium carbonate, and the solution diluted to 60 c.c. and cooled to 0°. A neutral solution containing 3 per cent. of potassium permanganate was then run in slowly while a rapid stream of carbon dioxide was passed through the alkaline liquid. The colour of the permanganate became permanent after the addition of an amount corresponding with one atom of available oxygen, and therefore a further quantity, corresponding with three atoms of oxygen, was gradually added, and the solution allowed to remain at room temperature for sixteen hours, after which decolorisation was complete. The solution was boiled and filtered, and the precipitated oxides of manganese extracted twice with boiling water. The aqueous solutions were combined and concentrated, then neutralised by means of concentrated hydrochloric acid, and rendered alkaline with ammonia. After boiling, a solution of calcium chloride was added, and the precipitate of calcium oxalate was collected and identified by the usual methods. The filtrate was strongly acidified and extracted five times with ether.

Dimethylmalonic Acid, $CMe_2(CO_2H)_2$.

The extract, on evaporation to a small bulk, deposited 0·3 gram of a colourless acid crystallising in well-defined, bevelled prisms. After recrystallisation from water, the acid melted at 189°. It was identified as dimethylmalonic acid by its characteristic crystalline form, melting point, and empirical composition (Found : C = 45·4 ; H = 6·1. Calc., C = 45·4 ; H = 6·1 per cent.).

Formation of Teraconic Acid (Dimethylitaconic Acid, XII) *from Dimethylaconitic Acid by Heating with Water.*

Dimethylaconitic acid (1 gram) was heated with a small quantity of water in a sealed tube at 180° for one hour. On cooling, long,

colourless prisms separated. After recrystallisation from water, these melted, when slowly heated, at 154—156°, but when heated rapidly, above 160°. The yield was rather small, and although several attempts were made, it could not be improved. The properties of the acid agreed closely with the description of teraconic acid (dimethylitaconic acid) given by Ssemenoff (*J. Russ. Phys. Chem. Soc.*, 1898, **23**, 430), and we do not doubt its identity. Unfortunately, however, an attempt which was made to bring about its conversion into terebic acid by heating with moderately concentrated sulphuric acid did not proceed well, and we were unable to repeat the experiment for lack of material (Found : C = 53·1 ; H = 6·4. $C_7H_{10}O_4$ requires C = 53·1 ; H = 6·4 per cent.).

(D) *Reduction of* 5 : 5-*Dimethyl*dicyclo*pentan*-3-*one*-1 : 2-*dicarboxylic Acid by Sodium Amalgam : Formation of* 5 : 5-*Dimethyl*cyclo*pentan*-3-*one*-1-*carboxylic Acid* (XVII) *and* 5 : 5-*Dimethyl*cyclo*pentan*-3-*ol*-1 : 2-*dicarboxylic Acid* (XX).

The primary reduction product of dimethyl*dicyclo*pentanonedicarboxylic acid is dimethyl*cyclo*pentanonedicarboxylic acid, which on liberation from its salts loses a carboxyl group as carbon dioxide and gives the ketonic monobasic acid. This, on further reduction, yields the monobasic hydroxy-acid, but if the original dibasic acid be reduced with excess of amalgam in a solution which is allowed to remain alkaline throughout the process, no elimination of a carboxyl group occurs, and the product is the *cyclo*pentane dibasic hydroxy-acid.

5 : 5-*Dimethyl*cyclo*pentan*-3-*one*-1-*carboxylic Acid* (XVII).

5 : 5-Dimethyl*dicyclo*pentan-3-one-1 : 2-dicarboxylic acid (4 grams) was dissolved in a slight excess of aqueous sodium carbonate solution, and the solution, diluted to 60 c.c., was saturated with carbon dioxide and cooled until about the half was frozen. The sodium amalgam (60 grams of 3 per cent.) was then added, and the mixture shaken continuously for half an hour while a current of carbon dioxide was passed and the temperature was maintained at the freezing point. The aqueous solution was filtered, acidified, and, after the brisk effervescence had subsided, rendered alkaline with ammonia and boiled. On adding a solution of barium chloride, any unchanged dimethyl*dicyclo*pentanonedicarboxylic acid was precipitated as its insoluble barium salt along with a certain quantity of barium carbonate. The filtered solution, on concentration, acidification by means of hydrochloric acid, and extraction with

ether, yielded 2·4 grams of a colourless syrup, which, when touched with a glass rod, completely solidified to a crystalline mass melting, without purification, at 100—103°. The substance, which separated from water in long, slender prisms, m. p. 103°, was identified as dimethyl*cyclo*pentanonecarboxylic acid by analysis (Found : C = 62·0; H = 7·9. Calc., C = 61·5; H = 7·7 per cent.), by its melting point, by the melting point of its semicarbazone (215°), and by direct comparison with a genuine specimen.

5 : 5-*Dimethyl*cyclo*pentan-3-ol-*1 : 2-*dicarboxylic Acid* (XX).

5 : 5-Dimethyl*dicyclo*pentan-3-one-1 : 2-dicarboxylic acid (5 grams) was dissolved in a slight excess of sodium carbonate solution in a shallow, flat-bottomed dish. A stream of carbon dioxide was bubbled continuously through the solution, and 10 grams of 3 per cent. sodium amalgam were added every half hour for twelve hours. The aqueous solution was then separated, rendered acid by means of hydrochloric acid, and extracted repeatedly with ether. By this means a good yield of a colourless acid was obtained, which, after recrystallisation from water, melted at 206° [Found : C = 53·9; H = 7·1. $C_9H_{14}O_5$ requires C = 53·4; H = 6·9 per cent. By titration : *M* (dibasic) = 204. Calc., *M* = 202].

(E) *Halogenation of* 5 : 5-*Dimethyl*dicyclo*pentan-3-one-*1-*carboxylic Acid and* 5 : 5-*Dimethyl*dicyclo*pentan-3-one-*1 : 2-*dicarboxylic Acid : Formation of the* 2-*Bromo-*, 2 : 4-*Dibromo-*, 2-*Chloro-*, 2 : 4-*Dichloro-*, *and* 2 : 2 : 4-*Trichloro-substitution Products of* 5 : 5-*Dimethyl*dicyclo*pentan-3-one-*1-*carboxylic Acid.*

Note on the Bromination of the Monobasic Acid.—The following experiments were conducted in order to ascertain whether the bromination process was one of substitution or of addition.

5 : 5-Dimethyl*dicyclo*pentan-3-one-1-carboxylic acid (1 mol.) was dissolved in chloroform, and a chloroform solution containing exactly two atomic proportions of bromine was added drop by drop, the mixture being kept at room temperature and shaken continuously during the addition. Hydrogen bromide was evolved during the later stages of the reaction, or, if a small amount of solvent were used, soon after the commencement. The generation of hydrogen bromide in solution took place from the beginning, and appeared to catalyse the process, for the colour of the first few drops of bromine solution disappeared only after several minutes, whilst in the later stages decolorisation was much more rapid. The resulting solution, which was almost colourless, was evaporated by leaving it in

an open basin in a strong draught. During this process further large quantities of hydrogen bromide were expelled, and there remained a white, crystalline cake, which, after keeping for some few hours in an evacuated desiccator over potassium hydroxide, was weighed, thoroughly ground in a mortar, and analysed. Three brominations, conducted in this way, gave the following figures :

	Grams of acid brominated.	Grams of product.	Bromine per cent.
First experiment	2	2·95	33·6
Second ,, ...	,,	2·92	33·7
Third ,, ...	,,	2·90	33·2
Theoretical results :			
(*a*) Assuming substitution to occur		3·02	34·3
(*b*) Assuming addition ,, ...		4·08	51·0

Similar experiments were carried out with four atomic proportions of bromine in place of two. As before, much hydrogen bromide was generated, and a white, crystalline mass was obtained, which was thoroughly ground before sampling for analysis. The results were as follows :

	Grams of acid brominated.	Grams of product.	Bromine per cent.
Fourth experiment	2	3·92	47·1
Fifth ,, ...	,,	3·95	49·8
Theoretical results :			
(*a*) Assuming substitution to occur		4·05	51·3
(*b*) Assuming addition of two atoms and substitution of two atoms		6·13	67·8

2-*Bromo*-5 : 5-*dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (XXVIII).

The products of the first, second, and third experiments consisted almost entirely of this bromo-acid, which was obtained in the pure condition by crystallisation from benzene, or by precipitation by means of water from a solution in acetic acid. It separated in stout needles or in leaflets, m. p. 154—155° (Found : C = 41·6; H = 3·9; Br = 33·8. $C_8H_9O_3Br$ requires C = 41·2; H = 3·9; Br = 34·3 per cent.). The action of dilute alkalis on this substance is described in section F.

2 : 4-*Dibromo*-5 : 5-*dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (XLIV).

The crude products of the fourth and fifth experiments (above) gave, on precipitation by means of water from a solution in acetic

acid, the pure dibromo-acid in 80 per cent. yield. It crystallised in lustrous leaflets, m. p. 164° (Found : C = 31·1 ; H = 2·7 ; Br = 51·4. $C_8H_8O_3Br_2$ requires C = 30·8 ; H = 2·6 ; Br = 51·3 per cent.).

Note on the Chlorination of the Mono- and Di-basic Acids.— Experiments were made with the object of successively mono- and di-chlorinating the monobasic acid by methods similar to the mono- and di-bromination processes described above; but, unfortunately, owing to the slight solubility of the acid in the usual organic solvents, the readily soluble, lower halogen derivatives were converted into more highly chlorinated products before the whole of the original acid had passed into solution. The mixtures of chlorination products proved exceedingly difficult to separate into their constituents, and no specimen of undoubtedly pure monochloro-acid was obtained. This acid was, however, prepared in small amount from the dibasic acid (which loses a carboxyl group as carbon dioxide on chlorination) by means of a strictly limited quantity of chlorine.

Similar difficulties were encountered in an endeavour to isolate the dichloro-acid from the products of chlorination of the dibasic acid; for, when the correct amount of chlorine was employed, mixtures were obtained from which a certain quantity of unchanged dibasic acid and the trichloro-derivative of the monobasic acid were somewhat easily separated. The residual mixture resisted repeated attempts to separate it by fractional crystallisation, and, although it almost certainly contained the monochloro-compound, the presence or absence of notable quantities of the dichloro-acid could not definitely be ascertained.

*2-Chloro-5 : 5-dimethyl*dicyclo*pentan-3-one-1-carboxylic Acid* (XXI).

This acid was prepared by passing chlorine (1 mol.) through a suspension of 5 : 5-dimethyl*dicyclo*pentan-3-one-1 : 2-dicarboxylic acid in chloroform, or by shaking the acid with the calculated quantity of a chloroform solution of chlorine. Most of the original acid (but not all) passed into solution, and carbon dioxide was generated. The solution having been filtered, the solvent evaporated, and the solid residue washed with a little water, a product was obtained which, after fractional crystallisation from benzene, yielded colourless, slender prisms, m. p. 183°. This consisted of 2-chloro-5 : 5-dimethyl*dicyclo*pentan-3-one-1-carboxylic acid (Found : C = 50·9 ; H = 4·7 ; Cl = 19·0. $C_8H_9O_3Cl$ requires C = 50·9 ; H = 4·8 ; Cl = 18·8 per cent.).

2 : 4-*Dichloro*-5 : 5-*dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (XXII).

This acid, which was first obtained as a by-product in the preparation of the oximino-derivative by the action of nitrosyl chloride on dimethyl*dicyclo*pentanonecarboxylic acid, was subsequently prepared by the following more convenient process.

The monocarboxylic acid was suspended in chloroform and treated with a stream of dry chlorine until a clear solution was obtained. The current of gas was then stopped and the solution kept in a cool place for several hours, in the course of which long, silky needles separated. These were collected and recrystallised first from benzene, then from dilute acetic acid, and finally from benzene. The pure substance formed colourless prisms, m. p. 173—174° (Found : C = 42·85; H = 3·6; Cl = 32·1. $C_8H_8O_3Cl_2$ requires C = 43·0; H = 3·6; Cl = 31·8 per cent.).

The hydrolysis of this substance by dilute alkalis is described in section F.

2 : 2 : 4-*Trichloro*-5 : 5-*dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (XXIII).

The trichloro-acid was obtained as a more soluble by-product in the preparation of the dichloro-acid (above), but was more conveniently prepared by passing a large excess of chlorine through a suspension of dimethyl*dicyclo*pentanonedicarboxylic acid in dry chloroform. During the process, the acid, which is only sparingly soluble in chloroform, gradually dissolved. Three hours after dissolution was complete the solvent was evaporated in a current of air, and the solid residue washed witb water, dried on porous porcelain, and crystallised from light petroleum (b. p. 60—70°). The pure trichloro-acid separated in colourless, rhomboidal plates, m. p. 127° (Found : C = 36·9; H = 2·8; Cl = 40·9. $C_8H_7O_3Cl_3$ requires C = 37·3; H = 2·7; Cl = 41·3 per cent.).

The decompositions which tbis substance undergoes in the presence of dilute alkalis is described in section F.

(F) *Action of Dilute Alkalis on the* 2-*Bromo*-, 2 : 4-*Dichloro*-, *and* 2 : 2 : 4-*Trichloro-derivatives of* 5 : 5-*Dimethyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid : Formation of* 5 : 5-*Dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one and its* 2-*Chloro*- *and* 4-*Chloro-substitution Products*.

Method of Hydrolysis.—The halogen derivative was boiled for a short time (one hour in the case of the chloro-compounds, and two

hours in the case of the bromo-acid) with 4 molecules of 5 per cent aqueous potassium hydroxide, and the deeply coloured liquid, which while hot, had a strong ketonic odour, was cooled and extracted twice with ether, which removed the substance having the odour. The alkaline liquid, on acidification, evolved carbon dioxide, and, on extraction with ether, yielded the *cyclo*pentenolone derivative.

5 : 5-*Dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one* (XXVI).

Crude dimethyl*cyclo*pentenolone was obtained from 2-bromo-5 : 5-dimethyl*dicyclo*pentan-3-one-1-carboxylic acid as an oil which quickly solidified, and was easily freed from some oily impurities by triturating with a mixture of dry ether and light petroleum (2 : 1 by volume), in which the crystals remained undissolved. The solid obtained in this way was almost colourless, and, when crystallised from ether, yielded large, well-formed prisms, m. p. 97°.

The substance proved to be a bromine-free, monobasic acid, which liberated carbon dioxide from sodium hydrogen carbonate and gave an intense red coloration with aqueous-alcoholic ferric chloride. It readily dissolved in warm water, benzene, or ether, and crystallised from a concentrated aqueous solution in large, well-defined, colourless prisms [Found: C = 66·8; H = 7·9. $C_7H_{10}O_2$ requires C = 66·7; H = 7·9 per cent. By titration: *M* (monobasic) = 126. Calc., *M* = 126].

4-*Chloro*-5 : 5-*dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one* (XXIX).

This substance was obtained by the action of 5 per cent. aqueous potassium hydroxide on 2 : 4-dichloro-5 : 5-dimethyl*dicyclo*pentan-3-one-1-carboxylic acid. The crude product of the hydrolysis (1·25 grams of an impure solid from 2·2 grams of the original dichloro-acid) was redissolved in sufficient ether, to which was then added half its volume of light petroleum. On keeping the solution at 0° for some time, the pure chlorodimethyl*cyclo*pentenolone crystallised in well-developed prisms, m. p. 122°. The yield was 50 per cent. of the theoretical.

The substance contained chlorine, and was strongly acidic, titrating as a monobasic acid. With ferric chloride in aqueous-alcoholic solution it yielded an intense red coloration. It was easily soluble in organic solvents (excepting light petroleum) and in water [Found: C = 52·4; H = 5·7; Cl = 22·2. $C_7H_9O_2Cl$ requires C = 52·3; H = 5·7; Cl = 22·1 per cent. By titration: *M* (monobasic) = 159·5. Calc., *M* = 160·5].

2-*Chloro*-5 : 5-*dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one* (XXX).

The crude product obtained from the trichloro-derivative of 5 : 5-dimethyl*dicyclo*pentanonecarboxylic acid (see general method, above) was washed with dry ether and crystallised from boiling water, from which it separated in colourless needles, m. p. 213°.

This substance gave an intense red coloration with aqueous-alcoholic ferric chloride, and was strongly acidic in character, titrating quite sharply as a monobasic acid [Found: C = 52·2; H = 5·65; Cl = 21·9. $C_7H_9O_2Cl$ requires C = 52·3; H = 5·65; Cl = 22·1 per cent. By titration, M (monobasic) = 158·5. Calc., M = 160·5].

The formation of this substance by chlorination of dimethyl*cyclo*pentenolone is mentioned on p. 158.

Oxidation of 5 : 5-*Dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one by means of Alkaline Hypochlorite : Formation of* as-*Dimethylsuccinic Acid and Chloroform.*

The dimethyl*cyclo*pentenolone was dissolved in a little aqueous potassium hydroxide and the solution added gradually and with continuous stirring to an alkaline solution of sodium hypochlorite (3·5 mols.) which was kept meanwhile at 0°. After half an hour, the separation of chloroform was complete, and the solution was acidified with hydrochloric acid and extracted with ether. The residue obtained on evaporating the ether quickly solidified, and was crystallised by dissolving it in a small amount of water and saturating the solution at 0° with hydrogen chloride. It separated in colourless prisms which melted at 140°, and was identified as *as*-dimethylsuccinic acid by a mixed-melting point determination with an authentic specimen and by analysis (Found: C = 49·4; H = 6·6. Calc., C = 49·3; H = 6·8 per cent.). The yield was almost quantitative.

Oxidation of 4-*Chloro*-5 : 5-*dimethyl*-Δ^1-cyclo*penten*-1-*ol*-3-*one by means of Alkaline Hypochlorite : Formation of Chloro*-as-*dimethylsuccinic Acid and Chloroform.*

This oxidation was conducted like the preceding and with similar results, chloroform separating out, as is usual in this type of reaction. The solid acid extracted by ether was contaminated with some gummy substance, and had to be purified by draining on porous porcelain and precipitation from its solution in benzene by means of light petroleum before it could be satisfactorily crystallised by dissolving it in water and saturating the well-cooled solution with hydrogen chloride.

Chloro-as-dimethylsuccinic Hydroxyanhydride (LI).

The pure substance took the form of a colourless, coarsely crystalline powder, melting at 140°, and readily soluble in water, benzene, chloroform, ethyl acetate, or dry ether. It dissolved readily in aqueous sodium hydrogen carbonate solution with effervescence, and contained chlorine, and was thought at first to be the expected chlorodimethylsuccinic acid; but an analysis showed that it was actually the anhydride of this substance (Found: C = 44·31; H = 4·25. $C_6H_7O_3Cl$ requires C = 44·34; H = 4·34 per cent.). The liberation of carbon dioxide from a bicarbonate was evidently not due to the fission of the anhydride ring, since the substance, when dissolved in water, titrated as a monobasic (not a dibasic) acid. Moreover, it gave a deep red colour with ferric chloride, a reaction shown by the hydroxy-anhydrides of the glutaconic acid series.

*Formation of 2-Chloro-5 : 5-dimethyl-Δ^1-*cyclo*penten-1-ol-3-one by Direct Chlorination of 5 : 5-Dimethyl-Δ^1-*cyclo*penten-1-ol-3-one.*

Dimethyl*cyclo*pentenolone (0·2 gram) was dissolved in 2 c.c. of a 5 per cent. aqueous solution of potassium hydroxide, and the solution was then added all at once to 8·8 c.c. of a hypochlorite solution containing 15·35 grams of total chlorine and 27 grams of sodium hydroxide per litre. Immediately the addition was made, the mixture was shaken vigorously and was then kept for five minutes. On adding sodium sulphite and acidifying by means of dilute sulphuric acid, the chloro-compound commenced to separate, but it was extracted with ether, from which, after drying and concentrating, it crystallised in colourless prisms. The substance was quite pure and melted at 213°; it was acidic and gave a deep red coloration with ferric chloride, and direct comparison with the chlorodimethyl*cyclo*pentenolone obtained by hydrolysis of the trichlorodimethyl*dicyclo*pentanonecarboxylic acid showed that the two were identical, as a mixed-melting point determination also proved. The yield was almost quantitative (Found: C = 52·2; H = 5·6. Calc., C = 52·3; H = 5·65 per cent.).

(G) *Monobromination of 5 : 5-Dimethyl*cyclo*pentan-3-one-2-carboxylic Acid: Formation of Monobromo-derivatives.*

Six grams of dimethyl*cyclo*pentanonecarboxylic acid (p. 151) were dissolved in chloroform and treated with a chloroform solution containing two atomic proportions of bromine. The bromine

solution was added drop by drop to keep pace with the absorption of the halogen, and the flask was continuously shaken during the process. Hydrogen bromide was evolved, and, on evaporating the solvent in a current of air, a semi-solid residue was obtained which solidified completely when kept in an evacuated desiccator over potassium hydroxide. The yield of crude solid was 9·2 grams (theoretical yield : 9·1 grams).

The crude solid was dissolved in boiling benzene, from which, after clarifying by pouring through a filter, and cooling, a substance crystallised in lustrous flakes (A). After a further crop of the same substance had been obtained from the mother-liquors by concentration, the residual solution was evaporated completely. The product thus obtained was not completely crystalline, but became so when left in contact with a little water for several hours. It was then dried, and, after a further quantity of the substance crystallising in flakes had been separated by means of benzene, was dissolved in hot water, and from the solution radial groups of stout, colourless prisms (B) were obtained.

The *Bromo-acid* (*A*).—The flaky substance, after a further crystallisation from benzene, melted at 170°, but was not quite pure. Final purification was effected by crystallisation from water, from which well-formed, slender prisms melting at 175° were obtained (Found : C = 40·7 ; H = 4·8 ; Br = 33·5. $C_8H_{11}O_3Br$ requires C = 40·8 ; H = 4·7 ; Br = 33·8 per cent.).

The *Bromo-acid* (*B*).—The substance that was more soluble in benzene, after a second crystallisation from water, separated in stout, colourless prisms, m. p. 125° (Found : C = 41·1 ; H = 4·7 ; Br = 34·0. $C_8H_{11}O_3Br$ requires C = 40·8 ; H = 4·7 ; Br = 33·8 per cent.).

Endeavours have been made to establish the constitutions of these bromo-acids by oxidation, and to eliminate the elements of hydrogen bromide from them by treatment with alkalis and organic bases. So far no recognisable products have been obtained, but the experiments have not been abandoned.

We desire to thank the Chemical Society for defraying a large proportion of the cost of this research.

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SOUTH KENSINGTON, S.W.7. [*Received, November 23rd*, 1921.]

XX.—*Researches on Residual Affinity and Co-ordination. Part VII. Cobaltic Lakes of the Alizarin Series.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN a recent communication on the cobaltammine lakes of the quinoneoxime or nitrosophenol dyes, we showed that the simple relationship existing between the number of cobalt atoms, n, and ammonia groups, m, present in these complex lakes could be represented by the equation $m = 5(n - 1)$ (T., 1921, **119**, 1066).

It was inferred from this generalisation that the quinoneoxime group had satisfied completely both the principal and supplementary valencies of one cobalt atom, so that this atom was no longer capable of combining with ammonia to form a cobaltammine co-ordination complex. This property of co-ordination was, however, retained by other cobalt atoms present in the lakes when these atoms had replaced the hydrogens of hydroxyl, carboxyl, or sulphonyl groups.

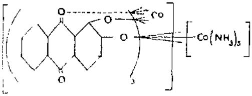
The disappearance of the residual affinity of the cobalt atom when implicated in the nitroso-complex is experimental evidence in support of the view that each of these so-called chelate groups functions as two associating units, so that three of them give the required number of six associating units to make up the maximum co-ordination number for the cobaltic atom.

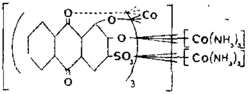
The promising results obtained with the quinoneoxime dyes suggested a method based on the cobaltammine reaction for distinguishing between ordinary salt-forming groups and the chelate complexes which confer on mordant dyes their characteristic lake-forming properties. We have accordingly extended the method to a representative series of the important alizarin dyes, which were kindly placed at our disposal by Mr. W. H. Dawson, of the British Alizarine Company, to whom we desire to express our cordial thanks.

Alizarin, when treated with the cobaltammine reagent, gives rise to a complex cobaltic lake containing two cobalt atoms and five ammonia groups as represented by formula I.

3-Nitroalizarin reacts in a similar manner, giving rise to a complex lake (II), the stability of which is increased by the introduction of the nitro-group.

The accumulation of hydroxyl groups in the alizarin molecule does not at first affect the type of complex lake produced. Flavo-

1 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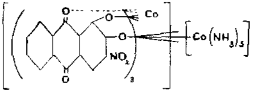

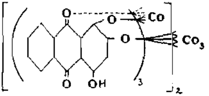
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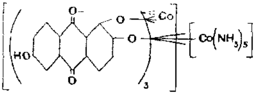

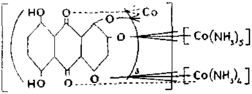
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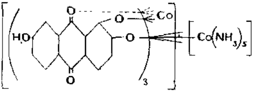

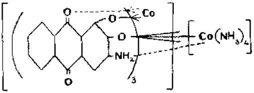
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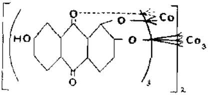

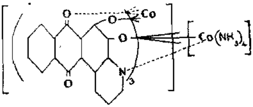
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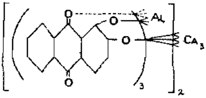
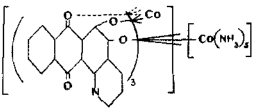
I 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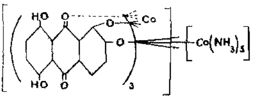


purpurin (6-hydroxyalizarin) gives the dicobaltic compound (III); but its isomeride, *iso*purpurin (anthrapurpurin or 7-hydroxyalizarin) does not react so smoothly; the 7-hydroxy-group tends to become reactive and mixed lakes are formed containing two and three cobalt atoms with five and ten molecules of ammonia respectively, and although it was not found possible to carry to completion the formation of a tricobaltic lake, yet by suitably regulating the proportions of cobalt and ammonia in the reagents a product was obtained consisting mainly of the dicobaltic lake (IV).

Further confirmation of the chelate structure was obtained in this more difficult case by the preparation of the simpler cobaltous cobaltic lake (V), and it is of interest to note that in this compound only the chelate complex is co-ordinated with triadic cobalt, although sufficient hydrogen peroxide was used to oxidise the second cobalt atom to the tervalent condition if this state of combination had been possible in conjunction with a phenoxide group. This difference in the states of combination of the two cobalt atoms is quite in accordance with the general behaviour of the metal, the higher valency of which is most frequently exhibited in its co-ordinated compounds.

Another noteworthy feature about the cobaltous cobaltic lake (V) and the similar one (IX) from purpurin is that these two compounds are analogues of the ordinary Turkey red dye (VI) on wool, in which tervalent cobalt is replaced by aluminium and bivalent cobalt by calcium.

These results with the cobalt lakes confirm the analytical data obtained by Möhlau from the double lakes of alizarin with the metallic pairs Al_2–Ca_3, Cr_2–Ca_3, and Fe_2–Ca_3 (*Ber.*, 1913, **46**, 443).

The foregoing cobaltic lakes have one common property in spite of the variation in the number of hydroxyl groups. They all fall within the category of *monochelate mordant dyes*, that is, they are colouring matters containing only one co-ordinating chelate group. This condition persists in the case of the lake from alizarin Bordeaux (5 : 8-dihydroxyalizarin), for on treating this dye with excess of cobaltammine reagent the two additional hydroxyl groups in positions 5 and 8 remain unreactive and the cobaltammine lake (VII) resembles its forerunners in containing only two cobalt atoms. The greater reactivity of β-hydroxy- as compared with that of α-hydroxy-groups has already been noticed in the case of stannic lakes and other complexes by Pfeiffer (*Ber.*, 1911, **44**, 2653; *Annalen*, 1913, **398**, 137).

A monochelate structure of more complex type was obtained by the use of alizarin red S (alizarin-3-sulphonic acid), this dye giving a cobaltammine lake (VIII) containing three cobalt atoms.

So far these cobaltammine lakes of the alizarin series conform to the simple numerical relationship $m = 5(n - 1)$, discovered in the quinoneoxime group (*loc. cit.*).

With the accumulation of hydroxyl groups in the same ring, as in purpurin (4-hydroxyalizarin) and alizarin cyanine (4 : 5 : 8-trihydroxyalizarin), a new factor arises, namely, the possibility of the co-existence of two chelate groups within the same molecule.

The turning-point occurs at purpurin, for this dye exhibits a marked tendency to form the complex tricobaltic tetrammine pentammine lake $[R_3Co_3(NH_3)_5(NH_3)_4]$, although this was found to be invariably mixed with the simpler dicobaltic pentammine lake $[R_3Co_2(NH_3)_5]$, the proportion of the former in the mixture varying from 40 to 60 per cent. Towards cobalt salts in the presence of an oxidising agent purpurin behaves as a monochelate dye, yielding the cobaltous cobaltic lake (IX), another analogue of Turkey red on wool (VI).

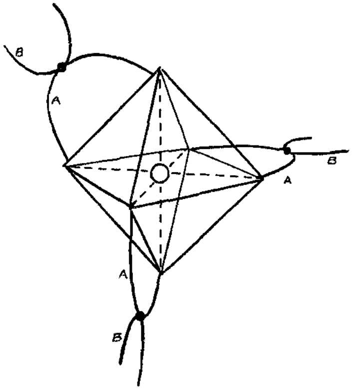
With alizarin cyanine, one reaches the definitely *dichelate mordant dyes*, for the cobaltammine lake (X) contains two ammine complexes, one with five and the other with four ammonia molecules. At this stage it is necessary to insist on the inadequacy of plane graphical formulæ to represent the steric relationships of the co-ordinating groups.

It would appear from the foregoing conventional formula to be quite possible for a second chelate complex consisting of the hydroxylic oxygen in position 4 and the remaining carbonyl group to co-ordinate so completely with the third cobalt atom that this atom would lose entirely its capacity for co-ordinating with ammonia. An inspection of a model (X*a*) of the lake constructed on the assumption that the first (alizarin) chelate group *A* is thrice co-ordinated at the vertices of the octahedral cobalt atom shows, however, that the remaining (purpurin) chelate group *B* cannot, owing to the spatial configuration of the lake, co-ordinate more than once with the third cobalt atom. This co-ordination with only one of three widely separated secondary chelate complexes leaves the third cobalt atom with four available positions in the co-ordination sphere and these become occupied by four ammonia molecules as indicated in formula X.

3-Nitroalizarin gives rise to a well-defined monochelate lake (II), the nitro-group exhibiting no residual affinity, but in 3-amino-alizarin the residual affinity of the amino-group leads to the development of a second chelate complex, the product being a *dichelate* lake (XI), in which the second cobalt atom co-ordinates with one of the three amino-groups and with four ammonia molecules.

Alizarin blue affords another example of a dichelate mordant dye, the second chelate complex containing the hydroxyl in position 2 and the quinoline nitrogen in position 3. The second cobalt atom replaces the hydrogens of the three hydroxyl groups and co-ordinates with one of the three tertiary nitrogens and four ammonia molecules, giving a dicobaltic quinoline-tetrammine lake (XII) of the purpureo-cobaltammine type.

If in the foregoing lake the dichelate structure is due to the implication of quinoline nitrogen in the cobaltammine complex, then a lateral inversion of the quinoline ring should destroy the



(Xa.)

second chelate group. This altered orientation of the quinoline nitrogen obtains in alizarin green M.L. & B., a closely related isomeride of alizarin blue.

An examination of the cobaltammine lake of this brand of alizarin green confirms our theoretical anticipation. The lake XIII contains cobalt and ammonia in the ratio 2Co : $5NH_3$; it is derived evidently not from a dichelate but from a monochelate dye.

These two lakes XII and XIII derived from isomeric dyes show very definitely the influence of orientation on the development of chelate groups. The only difference between the two isomeric dyes is due to a transference of quinoline nitrogen from an ortho- to a meta-position with respect to the β-hydroxyl group, but

this change is accompanied by a disappearance of the dichelate structure.

This study of the alizarin mordant dyes has revealed the co-existence of two chelate groups in the same colouring matter. The resulting modification in the composition of the cobaltammine lake follows a new rule, owing to steric hindrance operating against the threefold co-ordination of more than one chelate group in the same lake. The second chelate group co-ordinates only once with a second cobalt atom, leaving the latter partly free to co-ordinate with four ammonia molecules. These new conditions arising in the more complex case of dichelate dyes can also be summarised in a simple general equation

$$m = 5\left[n - \frac{(c + 4)}{5}\right],$$

expressing the number of ammonia molecules m, the cobalt atoms n and the chelate groups c. When c is unity, the simpler case of the monochelate dyes is represented and the equation reverts to its original form, $m = 5(n - 1)$.

The more general equation gives the composition of all the cobaltammine lakes described in this paper and in the preceding communication on quinoneoxime dyes (*loc. cit.*).

EXPERIMENTAL.

In the following preparations of cobaltammine lakes the following procedure was generally adopted :—

A. *Cobaltammine Reagent.*—2*N*-Cobalt chloride, 5*N*-ammonia, and 5*N*-hydrogen peroxide were mixed in such proportions that six molecules of ammonia and one half-molecule of hydrogen peroxide were present for every atom of cobalt :—20 c.c. of 2*N*-cobalt chloride (= 1·18 grams Co), 20 c.c. of 5*N*-ammonia (= 1·7 grams NH_3), and 10 c.c. of 20 vol. hydrogen peroxide.

B. The alizarin dye was dissolved or suspended in 5*N*-ammonia so that one molecule of ammonia was present for every hydroxyl or sulphonyl group in the dye.

Solutions A and B were mixed in such proportions that one-third of an atomic proportion of cobalt was present for every hydroxyl or sulphonyl group of the alizarin dye. The mixture was stirred mechanically for thirty minutes, warmed at 60° for the same time with the addition of a few c.c. of strong aqueous ammonia, and cooled in the ice-chest. The precipitated lake was washed successively with aqueous ammonia and water and dried in a vacuum over soda-lime.

I.—*Monochelate Alizarin Lakes.*

*2-Pentammino-*1 : *2-dicobaltic* 1 : *2-Dioxyanthraquinone* (I).—This alizarin lake, prepared from a 20 per cent. paste of alizarin red P, was a violet precipitate insoluble in water and dissolving very sparingly in dilute acids or alkalis and more readily in hot 5*N*-sodium hydroxide to a deep violet solution evolving ammonia; it developed a green coloration with 10*N*-hydrochloric acid, becoming pink on dilution: Found: Co = 13·0; NH_3 = 8·8. $[(C_{14}H_6O_4)_3Co][Co(NH_3)_5]$ requires Co = 12·9; NH_3 = 9·3 per cent.

*2-Pentammino-*1 : *2-dicobaltic* 1 : *2-Dioxy-3-nitroanthraquinone* (II). —This lake from 20 per cent. 3-nitroalizarin (alizarin orange paste) was almost insoluble in water, dilute acids, or alkalis; it dissolved in hot 5*N*-sodium hydroxide, evolving ammonia, and developed olive-green and transient blue colorations respectively with concentrated hydrochloric and sulphuric acids: Found: Co = 11·7; NH_3 = 8·3; N = 10·5. $[(C_{14}H_5O_6N)_3Co][Co(NH_3)_5]$ requires Co = 11·2; NH_3 = 8·1; N = 10·6 per cent.

*2-Pentammino-*1 : *2-dicobaltic* 1 : *2-Dioxy-6-hydroxyanthraquinone* (III).—Flavopurpurin (alizarin Y.C.A.) furnished a dark purple lake (yield 97 per cent.) sparingly soluble in water, dilute acids, and strongly alkaline solutions, soluble in hot sodium hydroxide, evolving ammonia. This lake was sparingly soluble in 5*N*-, but not in 18*N*-ammonia; with concentrated hydrochloric and sulphuric acids it developed green and violet colorations respectively: Found: Co = 11·8; NH_3 = 9·1. $[(C_{14}H_6O_5)_3Co][Co(NH_3)_5]$ requires Co = 12·2; NH_3 = 8·8 per cent.

*2-Pentammino-*1 : *2-dicobaltic* 1 : *2-Dioxy-7-hydroxyanthraquinone* (IV).—*iso*Purpurin (7-hydroxyalizarin) gave a reddish-violet lake which became purple on warming: Found: Co = 13·0; NH_3 = 8·4. $[(C_{10}H_6O_5)_3Co][Co(NH_3)_5]$ requires Co = 12·2; NH_3 = 8·8 per cent. It was only after many unsuccessful attempts that a lake of this composition was obtained. In other experiments this lake, $Co_2(NH_3)_5R_3$, was formed in mixtures containing also one or other of the following:—$Co_3(NH_3)_{10}R_3$, $Co_2(NH_3)_6R_3$, $Co(NH_4)_3R_3$, and $Co_2(NH_3)_5(NH_4)_3R_3$, where R is the *iso*purpurin residue. Confirmation of the nature of the *iso*purpurin lakes was obtained by preparing a cobalt compound not containing ammonia.

2-Cobaltous 1-*Cobaltic* 1 : *2-Dioxy-7-hydroxyanthraquinone* (V).—*iso*Purpurin (7·7 grams), ground up with 50 c.c. of *N*-sodium hydroxide, was treated successively with 25 c.c. of 2*N*-cobalt chloride (1·475 Co) and 8 c.c. of 5*N*-hydrogen peroxide, and the mixture heated on the water-bath for thirty minutes. The precipitate, washed successively with a few c.c. of very dilute acid

and water, was dried over concentrated sulphuric acid and extracted with ether in a Soxhlet apparatus until all unchanged *iso*purpurin had been removed. Acids decomposed the lake, and on diluting its solution in concentrated sulphuric acid *iso*purpurin separated: Found: Co = 16·3; *iso*purpurin = 83·9. $[(C_{14}H_6O_5)_3Co]_2Co_3$ requires Co = 16·2; *iso*purpurin = 84·4 per cent.

This cobaltous cobaltic lake developed intense magenta and green colorations with hot pyridine and 10*N*-hydrochloric acid respectively.

2-*Pentammino*-1 : 2-*dicobaltic* 1 : 2-*Dioxy*-5 : 8-*dihydroxyanthraquinone* (VII).—Alizarin Bordeaux (5 : 8-dihydroxyalizarin) furnished a practically quantitative yield of the dark blue lake having a bronzy lustre. This substance was insoluble in water; it dissolved only sparingly in dilute acids or alkalis and evolved ammonia in hot 5*N*-sodium hydroxide, giving an intense blue solution: Found: Co = 11·3; NH_3 = 8·2. $[(C_{14}H_6O_6)_3Co][Co(NH_3)_5]$ requires Co = 11·6; NH_3 = 8·4 per cent. In concentrated hydrochloric and sulphuric acids, the lake gave transient blue colorations turning to more purple shades; on dilution alizarin Bordeaux was precipitated.

2 : 3-*Dipentammino*-1 : 2 : 3-*tricobaltic* 1 : 2-*Dioxyanthraquinone*-3-*sulphonate* (VIII).—Alizarin-3-sulphonic acid (alizarin red S) gave a reddish-violet precipitate changing on warming to a dark purple lake sparingly soluble in water and dilute acids or alkalis: Found: Co = 13·2; NH_3 = 13·1; S = 7·0. $[(C_{14}H_5O_7S)_3Co][Co(NH_3)_5]_2$ requires Co = 13·6; NH_3 = 13·1; S = 7·4 per cent. The lake developed a green coloration with 10*N*-hydrochloric acid, and with concentrated sulphuric acid a transient blue coloration becoming purple and on dilution changing successively to green and orange.

2-*Cobaltous* 1-*Cobaltic* 1 : 2-*Dioxy*-4-*hydroxyanthraquinone* (IX).—As pointed out in the introduction (p. 163), 1 : 2 : 4-trihydroxyanthraquinone (purpurin) behaved in a somewhat anomalous manner. With the cobaltammine reagent it showed a tendency to react as a dichelate dye, giving rise to a mixture of 60 per cent of the monochelate lake $[Co_2(NH_3)_5R_3]$ with 40 per cent. of the dichelate lake $[Co_3(NH_3)_5(NH_3)_4R_3]$. By varying the proportions, the ratio of these two lakes was reversed, and, moreover, the employment of larger proportions of cobalt led to the production of mixed lakes containing cobaltous as well as cobaltic radicles. In the absence of ammonia, purpurin functions as a monochelate dye, yielding the cobaltous cobaltic lake analogous to the one from *iso*purpurin.

Purpurin (3·84 grams) was ground up with 25 c.c. of *N*-sodium hydroxide and heated for thirty minutes on the water-bath with

12·5 c.c. of 2*N*-cobalt chloride (= 0·74 gram Co) and 5 c.c. of 5*N*-hydrogen peroxide. The precipitate, after washing with dilute acetic acid and water, was dried and extracted with ether in a Soxhlet apparatus to remove unchanged purpurin: Found: Co = 15·9; purpurin = 83·3. $[(C_{14}H_6O_5)_3Co]_2Co_3$ requires Co = 16·2; purpurin = 84·4 per cent. The sparingly soluble lake dissolved in 5*N*-ammonia or sodium hydroxide to bluish-red solutions, the latter changing to orange on adding dilute acetic acid. Magenta, green and carmine colorations were developed with hot pyridine, 10*N*-hydrochloric acid, and concentrated sulphuric acid respectively. From the last of these solutions purpurin was precipitated on dilution.

2-*Pentammino*-1 : 2-*dicobaltic* 1 : 2-*Dioxyanthraquinone*-4-*quinoline* (XIII).—Owing to its sparing solubility in aqueous ammonia, alizarin green M.L. & B. was treated three times with excess of cobaltammine reagent. At each stage the olive-black lake was dried and analysed, when it gave successively the ratio Co : NH_3 as 2 : 5·14, 2 : 5·05, and 2 : 5·01. Found: Co = 10·4; NH_3 = 7·5; quinoline N = 3·4; total N = 9·3. $[(C_{17}H_7O_4N)_3Co][Co(NH_3)_5]$ requires Co = 11·0; NH_3 = 7·9; quinoline N = 3·9; total N = 10·5 per cent. This lake was insoluble in water, dilute acids, and cold aqueous alkalis, but dissolved in boiling 5*N*-sodium hydroxide to a dark green solution evolving ammonia. The purple solution of the lake in syrupy phosphoric acid became blood red on warming, purple on dilution, and changed to green with alkalis. Glacial acetic acid gave a green coloration becoming purple on boiling and showing green and purple dichroism on cooling.

II.—*Dichelate Alizarin Lakes.*

2-*Pentammino*-4-*tetrammino*-1 : 2 : 4-*tricobaltic* 1 : 2 : 4-*Trioxy*-5 : 8-*dihydroxyanthraquinone* (X).—Alizarin cyanine A.C. 10 per cent. paste (1 : 2 : 4 : 5 : 8-pentahydroxyanthraquinone) yielded a purplish-black lake insoluble in water and cold dilute acids or alkalis, dissolving in boiling 2*N*-hydrochloric acid to a red solution, whereas with the 10*N*-acid it developed an olive-green coloration. With concentrated sulphuric or syrupy phosphoric acid it developed a dark olive coloration changing to violet on warming and to carmine on dilution: Found: Co = 15·3; NH_3 = 13·1. $[(C_{14}H_5O_7)_3Co][Co(NH_3)_5][Co(NH_3)_4]$ requires Co = 14·9; NH_3 = 12·9 per cent.

2-*Tetrammino*-1 : 2-*dicobaltic* 1 : 2-*Dioxy*-3-*aminoanthraquinone* (XI).—From 3-aminoalizarin a dark purple lake was obtained insoluble in water and cold dilute acids or alkalis: Found: Co =

12·1; NH_3 = 7·0; N = 10·6. $[(C_{14}H_7O_4N)_3Co][Co(NH_3)_4]$ requires Co = 12·5; NH_3 = 7·2; N = 10·4 per cent.

This lake developed a yellowish-green coloration with 10*N*-hydrochloric acid and an intense brown colour with concentrated sulphuric acid, these solutions on dilution becoming yellow and reprecipitating 3-aminoalizarin.

*2-Tetrammino-*1 : *2-dicobaltic* 1 : *2-Dioxyanthraquinone-3-quinoline* (XII).—Alizarin blue A.B.I. (alizarin-3*N*-quinoline : Found : N = 4·6. Calc., N = 4·8 per cent.) gave a dark greenish-blue lake : Found : Co = 11·2; NH_3 = 6·4; quinoline N = 3·8; total N = 9·1. $[(C_{17}H_7O_4N)_3Co][Co(NH_3)_4]$ requires Co = 11·2; NH_3 = 6·5; quinoline N = 4·0; total N = 9·3 per cent.

This dichelate lake, although insoluble in cold dilute acids or alkalis, dissolved in hot 2*N*-hydrochloric acid to a pink solution becoming blue with ammonia and green with caustic alkali. The yellow solution in hot 5*N*-sodium hydroxide evolved ammonia and became green on boiling. Reddish-violet and intense blue colorations were developed with concentrated hydrochloric and snlphuric acids respectively. In syrupy phosphoric acid the lake dissolved to an intense reddish-violet solution becoming deep orange on warming and red on dilution.

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XXI.—*A Comparison of Three Isomeric Carbocyanines.*

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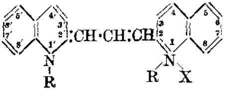
A LARGE number of representatives of these dyestuffs have been prepared, and the effect of introducing various substituents on their photosensitising action studied (Pope and Mills, *Phot. J.*, 1920, **60**, 253). Considerable interest also attaches to the determination of the result of varying the position in the molecule of a given substituent. Comparisons of this nature in the *iso*cyanine series have recently been published by Miss F. M. Hamer (T., 1921, **119**, 1432).

A consideration of the formula of the carbocyanines, established by Mills and Hamer (T., 1920, **117**, 1550), shows that several



isomerides are theoretically possible. In practice, however, their number is considerably lessened by the fact that only those in which the two quinoline nuclei are similarly substituted can conveniently be prepared. The present paper deals with the carbocyanines in which the ethoxyl group is present in the 5 : 5′-, 6 : 6′-, and 7 : 7′-positions.

The absorption spectra of these dyes in dilute alcoholic solution show two well-defined bands in the visible region, the less refrangible being the more intense. The sensitisation spectra, obtained by photographing the spectrum with a plate previously bathed in a dilute aqueous alcoholic solution of the dye, show, in addition to the broad band in the blue, extending into the ultra-violet, representing the sensitiveness of the normal gelatino-bromide plate, a second broad band having two maxima corresponding with the two absorption bands. As in the case of other photosensitising dyes, the sensitisation maxima are situated nearer the red end of the spectrum than the corresponding absorption bands. The latter, the general appearance of which is very similar in all three compounds, are situated nearest the red end in the 6 : 6′- and furthest from the red end in the 5 : 5′-derivative. An analogous variation is observed in the position of the less refrangible sensitisation maximum, whilst the position of the second appears to remain approximately constant. Accompanying this variation in the distance between the two sensitisation maxima, a very striking contraction of the breadth of the sensitisation bands is observed in the 5 : 5′-derivative, as compared with the 6 : 6′- and 7 : 7′-isomerides. A similar relation has been observed between the 5 : 5′- and 6 : 6′-dihromo-derivatives (Pope and Mills, *loc. cit.*), and Hamer points out (*loc. cit.*) that in the *iso*cyanines the effect of substitution is most marked in the 5-position.

EXPERIMENTAL.

6 : 6′-*Diethoxy*-1 : 1′-*diethylcarbocyanine Iodide.*

6-*Ethoxyquinaldine.*—To an ice-cooled mixture of concentrated hydrochloric acid (200 c.c.) and *p*-phenetidine (75 grams), in which

some of the hydrochloride had separated out in the solid state, acetaldehyde (80 c.c. of a 73 per cent. solution) was slowly added with mechanical stirring. The mixture was gradually warmed under reflux until spontaneous reaction set in, and gently boiled for a further three hours after this initial action had subsided. After cooling, water (1 litre) was added and the mixture kept for several hours. The solution was separated from precipitated tar, made alkaline with sodium hydroxide, and extracted with ether. The extract was dried with sodium carbonate, and the residue fractionally distilled under diminished pressure. The fraction boiling up to 165°/14 mm. comprised mainly unchanged *p*-phenetidine; that distilling between 165° and 180°/14 mm. (25—30 grams) solidified in the receiver. This 6-ethoxyquinaldine was pressed on porous tile to remove traces of oil, and recrystallised from petrol, giving shiny, colourless plates, m. p. 71° (Found: C = 76·7; H = 7·03; N = 7·37. $C_{12}H_{13}ON$ requires C = 77·0; H = 6·95; N = 7·49 per cent.).

6-*Ethoxyquinaldine Hydrate*.—On heating the base with boiling water and cooling the mixture, a small quantity of the hydrate separated as colourless needles. A better method of preparation of the hydrate was to heat a solution of the base in dilute alcohol at 100° for sixteen hours and to allow the resulting solution to evaporate slowly at room temperature. In this way, large, colourless plates were obtained, m. p. 58—59°. The hydrate lost 8·92 per cent. in weight when left in an evacuated desiccator; $C_{12}H_{13}ON,H_2O$ requires H_2O = 8·78 per cent. The residual solid melted at 71° and did not depress the m. p. of the anhydrous base.

6-*Ethoxyquinaldine Ethiodide*.—This, like the subsequent quaternary iodides, was obtained by heating the base with a slight excess of alkyl iodide for sixteen hours under reflux. The product was recrystallised from alcohol and dried by heating at 80° under a pressure of 11 mm. until the weight became constant. Yellow needles were obtained, m. p. 182° (Found: I = 36·83; $C_{14}H_{18}ONI$ requires I = 37·02 per cent.).

6-*Ethoxyquinaldine Picrate*.—Pale yellow needles, m. p. 192°.

6-*Ethoxyquinaldine Chromate*.—Golden-yellow needles, m. p. 145° (decomp.).

6-*Ethoxyquinaldine Hydrochloride*.—Small, colourless needles, m. p. 184—186°.

6 : 6′-*Diethoxy*-1 : 1′-*diethylcarbocyanine iodide* was prepared by heating together for fifteen minutes 6-ethoxyquinaldine ethiodide (11·5 grams), quinoline ethiodide (10 grams), and formaldehyde (2·65 grams) in alcoholic solution with sodium hydroxide obtained by dissolving sodium (0·92 gram) in rectified spirit. The quinoline

salt takes no direct part in the condensation, but improves the yield. The solid that separated on cooling was repeatedly extracted with small quantities of hot alcohol, and then with a little hot acetic acid, a dark red impurity being in this way removed. The sparingly soluble carbocyanine was finally purified by crystallisation from methyl alcohol, being obtained as minute needles having an olive-green lustre; m. p. 296° (decomp.) (Found: I = 22·27. $C_{29}H_{33}O_2N_2I$ requires I = 22·36 per cent.).

The extra-sensitisation shows two maxima at 6600 and 5800 Å. respectively. The maxima of the two absorption bands lie at 6220 and 5760 Å.

5 : 5′-*Diethoxy*-1 : 1′-*diethylcarbocyanine Iodide*.

5-*Ethoxyquinaldine*.—The Doebner-Miller synthesis, as just described for the preparation of 6-ethoxyquinaldine, did not afford a satisfactory method of obtaining the 5-isomeride. Condensation of *m*-phenetidine with acetaldehyde yielded, in addition to tarry matter, a substance which, on heating, decomposed into water and a mixture of secondary and tertiary bases, and may therefore be of the nature of an aldol base. The tertiary bases, after removal of the secondary by means of nitrous acid, comprised ethoxyquinaldines (Found: N = 7·32. $C_{12}H_{13}ON$ requires N = 7·49 per cent.); with picric acid they yielded a solid which, after repeated crystallisation, melted indefinitely at 190—193°, whereas the picrates from 5- and 7-ethoxyquinaldine melt at 206—207° and 213° respectively. The yields of this mixture of ethoxyquinaldines were not satisfactory.

5-Ethoxyquinaldine was prepared by the ethylation of 5-hydroxyquinaldine, the latter being obtained by heating 5-aminoquinaldine hydrochloride with excess of concentrated hydrochloric acid at 210—220° for six hours (compare the preparation of 5-hydroxyquinoline by Claus and Howitz, *J. pr. Chem.*, 1893, [ii], **47**, 432). The pure hydroxy-base was found to melt at 227—229°, as against 232—234°, the m. p. given by Doebner and von Miller (*Ber.*, 1884, **17**, 1709). Using the calculated quantities of sodium and ethyl iodide and warming the alcoholic mixture for five hours under reflux, a 77 per cent. yield of 5-ethoxyquinaldine was obtained. It forms a pale yellow, syrupy oil boiling at 174—175°/11 mm. or 290—292°/760 mm.; it did not solidify on cooling to − 8° (Found: N = 7·48. $C_{12}H_{13}ON$ requires N = 7·49 per cent.).

5-*Ethoxyquinaldine Ethiodide*.—Orange-yellow needles, m. p. 166° (Found: I = 36·94. $C_{14}H_{18}ONI$ requires I = 37·02 per cent.).

5-*Ethoxyquinaldine Picrate*.—Pale yellow needles, m. p. 206—207°.

5-*Ethoxyquinaldine Chromate*.—Yellow needles, m. p. 153° (decomp.).

5 : 5′-*Diethoxy*-1 : 1′-*diethylcarbocyanine Iodide*.—Minute crystals with an olive-green lustre, m. p. about 325° (decomp.) (Found: I = 22·45. $C_{29}H_{33}O_2N_2I$ requires I = 22·36 per cent.).

The extra-sensitisation is much more contracted than in the previous isomeride, and consists of two well-defined bands with maxima at 6250 and 5800 Å. respectively. The two absorption bands have maxima at 6030 and 5590 Å.

7 : 7′-*Diethoxy*-1 : 1′-*diethylcarbocyanine Iodide*.

7-*Ethoxyquinaldine*.—7-Aminoquinaldine was prepared by reducing 2 : 4-dinitrophenyl-lactyl methyl ketone with zinc and acetic acid. Its hydrochloride was converted by heating with concentrated hydrochloric acid, as described for the 5-isomeride, into the hydroxy-base. This compound crystallised from chloroform in colourless needles which darkened above 240° and melted at 246—247°; it sublimed when heated at 100° under diminished pressure (Found: N = 8·6. $C_{10}H_9ON$ requires N = 8·8 per cent.).

7-Ethoxyquinaldine, obtained by ethylation of the hydroxy-base, is a pale yellow, syrupy oil, boiling at 307—308°/770 mm.; it did not solidify when cooled to − 6° (Found: N = 7·31. $C_{12}H_{13}ON$ requires N = 7·49 per cent.).

7-*Ethoxyquinaldine Ethiodide*.—Yellow prisms, m. p. 216—218° (decomp.) (Found: I = 36·74. $C_{14}H_{18}ONI$ requires I = 37·02 per cent.).

7-*Ethoxyquinaldine Picrate*.—Pale yellow needles, m. p. 213°.

7 : 7′-*Diethoxy*-1 : 1′-*diethylcarbocyanine Iodide*.—Dark green needles with brassy lustre, m. p. about 315° (decomp.) (Found: I = 22·62. $C_{29}H_{33}O_2N_2I$ requires I = 22·36 per cent.).

The sensitisation bands are slightly broader than in the 6 : 6′-isomeride, with maxima at about 6450 and 5800 Å. respectively. The crests of the two absorption bands lie at 6170 and 5710 Å.

The above investigation was undertaken at the suggestion of Dr. W. H. Mills, to whom I am very grateful for his constant and invaluable advice. I desire also to thank Mr. F. J. Stoakley, who photographed the sensitisation and absorption spectra of the dyes described.

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XXII.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part III. Mercuric Fulminate.*

By Robert Crosbie Farmer.

Mercuric fulminate detonates very readily on heating. Hoitsema (*Z. physikal. Chem.*, 1896, **21**, 137) found that it could be caused to decompose without explosion by slow heating, but no measurements of the velocity were made, and his observations as to the nature of the products are not confirmed. The present work shows that under the conditions of the vacuum test described in Part I (T., 1920, **117**, 1432), mercuric fulminate undergoes a regulated decomposition. The velocity curves are, however, of a most unusual type. As shown by the curves given later, the first phase is a quiescent period, during which there is only a very slight evolution of gas. Taking a typical example of the ordinary brown mercuric fulminate at 80°, this quiescent period lasts for about eighty hours. Evolution of carbon dioxide then sets in and increases rapidly until it attains a velocity of about 0·25 c.c. per gram per hour, whereupon the rate remains fairly constant for some time. If the heating be continued, the velocity will increase gradually, notwithstanding the decrease in the quantity of fulminate, until ultimately the evolution of gas will cease almost abruptly, leaving an inert residue. The total gas evolved corresponds in the mean with 0·58 mol. per mol. of fulminate.

Other reactions are known in which an "incubation period" occurs, but in general such reactions, after having once started, accelerate rapidly and continuously, whereas in the present case a catalyst appears to come into existence very rapidly, and then to remain for a time almost constant in quantity.

"White fulmiuate," which is prepared with the aid of cupric chloride, behaves somewhat differently from the brown. Its initial quiescent period is considerably longer than that of brown fulminate; the commeucement of the gas-evolution is not so abrupt, and the subsequent decomposition proceeds with an acceleration, so that the velocity ultimately becomes greater than that of the brown fulminate.

Experiments at different temperatures gave a temperature coefficient of 1·12 to 1·13 per degree. The most convenient temperature for the measurements was 80°. The decomposition in a partial atmosphere of air or carbon dioxide did not differ materially from that in a vacuum.

Apart from the main decomposition with evolution of carbon dioxide, a very slow subsidiary decomposition also occurred, as was shown by measurements in a vessel containing soda-lime. This proceeded with a slight acceleration from the start, and did not show any break in the velocity curve.

The decomposition of white and of brown fulminate in presence of light at the ordinary temperature was also examined, and it was found that a slow decomposition occurred in the light, which did not take place in the dark.

To gain an insight into the somewhat remarkable type of reaction which occurred on heating, experiments were made on the conditions which affected the velocity. It was proved, first, that the mercuric fulminate did not contain any absorbent for the gas evolved. Numerous additions of other compounds to the mercury fulminate were made, but in most cases these did not materially modify the nature of the decomposition, although certain admixtures, such as strong acids, accelerated the gas-evolution. Alkaline substances had a retarding tendency. Mercury compounds did not affect the velocity much. Water had a strong retarding influence, possibly giving rise to fulminurate.

Extraction of the original fulminate with water or alcohol and subsequent drying did not affect the rate of decomposition. When mercuric fulminate was dissolved in potassium cyanide solution and reprecipitated, the type of curve was not materially altered, but the rate of decomposition was somewhat affected. Thus the difference between white and brown fulminate was much less marked after this treatment.

When the fulminate was heated to the point of incipient gas-evolution and cooled, it did not revert to its former condition, nor did the addition of fresh fulminate at this point modify the further course of the decomposition. On the other hand, extraction of the slightly decomposed fulminate with water or acetone removed the active catalyst to some extent, and delayed the further decomposition. Addition of the residue of a decomposed fulminate to fresh fulminate caused a marked increase in the rate of evolution of gas, showing the formation of a catalyst during the decomposition. The carbon dioxide was found to be without influence on the velocity.

The degree of subdivision had an important influence. Finely-ground fulminate decomposed more rapidly than the larger crystals. This is in agreement with the work of Hinshelwood and Bowen (*Phil. Mag.*, 1920, [vi], **40**, 569) on potassium permanganate, etc., and would appear to indicate surface decomposition (see also Robertson, T., 1921, **119**, 15), although it is to be observed that the increase in the rate of decomposition is not so great as would have been

expected from the increase of surface on grinding. A similar effect to that of grinding was obtained when the mercuric fulminate was compressed into pellets, the crystals being thus disintegrated.

It is of interest to compare the effect of subdivision on brown and white fulminates. In the case of brown fulminate, the quiescent period at 80° was shortened, but the velocity curve was otherwise almost unchanged. The effect of compressing white fulminate was to bring its decomposition curve almost into line with that of compressed brown fulminates, namely, to shorten the incubation period very considerably, and to make the outbreak of gas-evolution more abrupt.

Reviewing the evidence on the nature of the decomposition, the initial quiescent period is not due to absorption of the gas evolved; there is no indication of a retarding catalyst, and if the fulminate undergoes an intramolecular change, it shows no sign of reverting to its original condition on cooling. The subsequent outbreak of decomposition is certainly due to the formation of a catalyst which was not originally present, as shown by the extraction experiments. It remains unexplained why the velocity, after rising so rapidly from practically zero, does not maintain its acceleration. From the experiments showing to what a degree the rate of decomposition is affected by the physical condition, it appears possible that the surface decomposition sets a limit to the rate at which the catalyst can act, bnt in the later stages of decomposition the rate per gram of unchanged fulminate becomes very much greater. The addition of certain substances such as diphenylamine to mercuric fulminate gave curious effects, which are difficult to reconcile with any ordinary hypothesis.

EXPERIMENTAL.

The method used was that described by the author in Part 1 (*loc. cit.*). As the compound is very sensitive to heat and friction, and detonates with great violence, it was necessary to take precautions against explosion. The glass test-tubes were surrounded by steel tubes of a thickness which had been shown by experiment to withstand the detonation of the required quantity of fulminate. Explosions were encountered in a few instances, notably in endeavouring to find the velocities at higher temperatures in the determination of the temperature coefficient and in some experiments on admixtures.

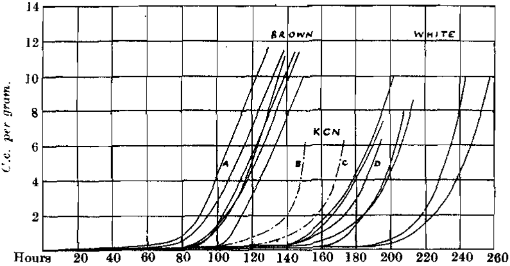
A temperature of 80° was found most suitable for the majority of the measurements. In general, there was practically no evolution of gas for the first period of several days, and decomposition then set in somewhat abruptly. On account of the abnormal type of the velocity curves, it is not convenient to compare the

volumes of gas after a given length of time as in previous instances (T., 1920, **117**, 1432, 1603); a much better comparison is obtained by recording the lengths of time necessary for a given evolution of gas, for example, 2 c.c. or 5 c.c. Each c.c. of gas corresponds with about 2·2 per cent. decomposition.

Comparison of Fulminates from Different Sources.—Fig. 1 shows a number of typical instances. These fall into two classes. Taking 1 gram at 80°, the ordinary brown fulminate shows a quiescent period of about eighty hours, and the decomposition then sets in somewhat abruptly, and continues with a fairly constant velocity. White fulminate shows a much longer quiescent period, and then begins to decompose with an acceleration, gradually attaining a velocity which is greater than that shown by the brown fulminates.

FIG. 1.

Decomposition of brown and white fulminates at 80°.



Influence of Temperature.—The general type of the velocity curves was similar at different temperatures, but at higher temperatures the initial quiescent period was shorter, and the subsequent velocity of decomposition was increased. At 100°, explosions were liable to occur, and no measurements were made above this temperature. The following table gives the values for a white and a brown fulminate.

Influence of Temperature.

I. Brown fulminate (1 gram).

Temperature	60·0°	70·4°	78·9°	79·8°	79·9°	80·1°	81·0°	89·6°	99·6°
	hours.	hours.	hours.	hours.	hours.	hours.	hours.	hours.	hours.
2 c.c.	1124	376	99·7	93·2	94·2	88·6	85·0	34·3	—
5 c.c.	1227	418	113·3	106·2	106·7	101·0	100·0	39·0	19·3
10 c.c.	1387	483	133·5	124·9	124·0	121·0	—	45·7	—

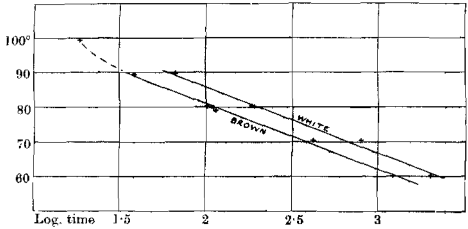
II. White fulminate (1 gram).

Temperature	60°	70·6°	80·0°	80·2°	89·6°
	hours.	hours.	hours.	hours.	hours.
2 c.c.	1897	750	175	170	62·0
5 c.c.	2010	795	189	182	67·2
10 c.c.	2096	826	—	—	70·8

Fig. 2 shows the relationship between the temperature and the logarithm of the time required for an evolution of 5 c.c. From this, the temperature coefficient is found to be 1·13 per degree. From

FIG. 2.

Influence of temperature on velocity.



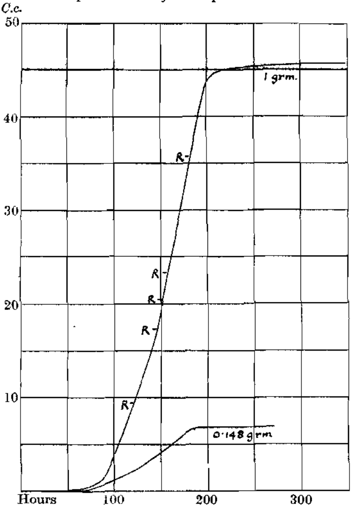
these and other determinations a mean temperature coefficient of 1·12 per degree or 1·75 per 5 degrees was obtained. A similar temperature coefficient is obtained on comparing the velocities of decomposition after the quiescent period.

Prolonged Heating of Mercuric Fulminate.—Fig. 3 shows the complete course of the decomposition of a brown fulminate. The two curves show respectively the decompositions of 1 gram and 0·148 gram of fulminate at 80°. The evolution of gas is proportional to the quantity of fulminate. It is seen that after the first quiescent period the decomposition proceeds at first with a nearly constant velocity, which increases slightly until the decomposition ultimately ceases almost abruptly. In order to ascertain whether the velocity was affected by the pressure of the gas, the tube was re-evacuated at intervals as shown by the points marked *R* in the curve. It is seen that the velocity was not affected by the re-evacuation.

Total Evolution of Gas from Brown and White Fulminates.—This is shown for a number of samples at 80° in the following table. The loss of weight was found to be the same at 100°.

Fig. 3.

Complete course of decomposition at 80°.



Total Evolution of Gas.

Sample No.	Original weight (grams).	Total gas (c.c. corr.).	C.c. per gram.	Mol. of gas per mol. of fulminate.	Loss of weight per cent.
Brown fulminates					
20	1·000	45·55	45·55	0·583	—
,,	0·148	6·73	45·5	0·582	—
24	1·0895	52·30	48·00	0·614	9·42
,,	2·090	—	—	—	9·52
,,	2·0573	—	—	—	9·21
,,	2·1694	—	—	—	9·02
,,	2·075	—	—	—	9·18
,,	0·2106	9·33	44·3	0·567	—
White fulminates					
37	0·1930	8·58	44·4	0·568	—
,,	0·6574	29·6	45·03	0·576	9·05
,, (large crystals)	0·096	4·44	46·25	0·592	—

The residue from the decomposition formed a brown, insoluble material, the particles of which had retained their original crystalline shape. The nature of the residue is being studied further.

The gas evolved was nearly pure carbon dioxide, and the loss of weight was in accordance with this. In the case of brown fulminate 52·3 c.c. of gas corresponded with a loss of weight of 0·1026 gram (CO_2 requires 0·1035). In the case of white fulminate, 29·6 c.c. weighed 0·0595 gram (CO_2 requires 0·0585).

When mercuric fulminate was heated in a tube containing soda-lime, separated from the fulminate by a layer of glass wool, the gas-evolution was reduced to a very low point. Prolonged heating showed, however, that apart from the evolution of carbon dioxide, a slow decomposition of a different type occurred, giving gases which were not absorbed by soda-lime.

Evolution of Gases other than Carbon Dioxide.

Brown fulminate No. 20. Quantity 2 grams. Temp. 80°.

Time (hours)	50	100	150	200	250	300	350	400
C.c. of gas	0·03	0·07	0·15	0·23	0·36	0·57	0·86	1·25

Experiments on Catalytic and Other Conditions.

(1) *Interruption after Incipient Gas Evolution.*—To gain information on the nature of the quiescent period it was necessary to ascertain whether the mercuric fulminate, after heating until the evolution of gas commenced, was capable of reverting to its original condition at a lower temperature.

This was not the case. In the experiment indicated by Fig. 4, curve 5, the heating at 80° was interrupted at the point shown by a break in the curve. The fulminate was then kept for some days at the ordinary temperature, and again heated at 80°. It is seen that the decomposition proceeded as if there had been no such interruption. Moreover, it has been found that the fulminate can pass through the same phases of incubation period and active decomposition at low temperatures : thus when very old fulminate is heated, it gives a decomposition represented by the latter part of the curve in Fig. 3.

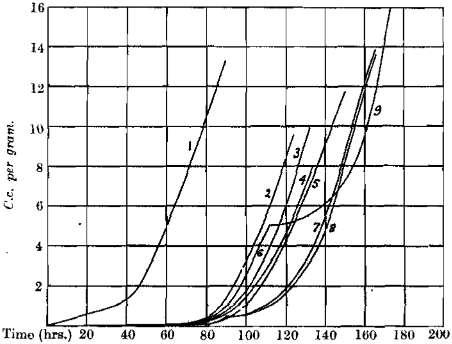
(2) *Mixture of Fulminate, after Incipient Decomposition, with Fresh Fulminate.*—Such a mixture was tested to ascertain whether the unheated fulminate contained an inhibiting catalyst, which would delay the further decomposition of the partly heated ful-

minate. In Fig. 4, curve 2, one gram of brown fulminate was heated at 80° to the point shown by a break in the curve. It was then cooled, and intimately mixed with 1 gram of fresh fulminate. On heating further, the evolution of gas continued as shown, without any retardation due to the addition of fresh fulminate. It must be admitted that the solid contact might in this case be insufficient to allow an inhibiting substance to exert its action.

(3) *Treatment of Fulminate with Carbon Dioxide.*—The above experiment shows that the initial quiescent period is not due to absorption of the carbon dioxide by the fulminate or any small

FIG. 4.

Experiments on catalysis.



quantity of foreign matter contained in it. This was confirmed by passing carbon dioxide over fulminate for some time. There was no gain in weight, and this treatment did not materially affect the decomposition curve. Curve 3 in Fig. 4 shows the gas-evolution from fulminate previously treated with carbon dioxide compared with the untreated sample (curve 4).

(4) *Decomposition in Presence of Air.*—Comparisons were made in which the fulminate was heated at 60° (1) in a vacuum, (2) under an air pressure of about 500 mm. The presence of air had only a minor influence on the velocity, as shown by the following figures.

Influence of Air.

Fulminate No. 24. Temperature 60°. Quantity 1 gram. Time of evolution in hours.

	1 c.c.	2 c.c.	3 c.c.	4 c.c.	5 c.c.	6 c.c.
In a vacuum	868	925	970	1006	1039	1069
,, ,, ...	842	900	944	983	1020	1053
500 mm. air pressure	945	1008	1052	1094	1135	—
,, ,, ,,	960	1026	1073	1115	1156	1193

(5) *Extraction with Alcohol.*—As mercuric fulminate is washed very thoroughly with water in the course of its manufacture, it follows that any catalyst which it contains (positive or negative) must be insoluble in water. A sample of the fulminate was extracted with alcohol to ascertain whether this would remove the catalyst, but the decomposition was not affected.

Extraction of White Fulminate with Alcohol.

Fulminate No. 89. Temperature 80°. Quantity 1 gram. Time of evolution in hours.

	1 c.c.	2 c.c.	3 c.c.	4 c.c.	5 c.c.	10 c.c.
Before extraction ...	208	217	223	227	231	243
After extraction ...	210	219	224	228	231	243

(6) *Solution in Cyanide and Reprecipitation.*—Samples were dissolved in potassium cyanide and reprecipitated. The effect of this treatment on brown and white fulminates is shown in Fig. 1. Curves *A* and *D* show a brown and a white fulminate respectively before treatment, and curves *B* and *C* the same fulminates after treatment (1 gram at 80°). It is seen that the brown and the white fulminate are brought much nearer together, but the type of curve remains essentially unchanged, insofar as there is still an incubation period. This speaks against the presence of an impurity acting as an inhibiting agent.

(7) *Extraction with Solvents after Partial Decomposition.*—A sample of fulminate (1 gram) was heated to incipient gas-evolution. After ninety hours, it had evolved 0·5 c.c. of gas. Portions were then extracted for four days with cold water and acetone respectively, to ascertain whether the catalyst would be removed and the further decomposition retarded. In Fig. 4, curves 7 and 8, the portion up to ninety hours from the start represents the original heating. Curve 8 shows the continuation of the decomposition in c.c. per gram after extraction with water and curve 7 after extraction with acetone. This shows that the accelerating catalyst was removed to some extent by the extractions. In a further experi-

ment (curve 6) the original fulminate was heated until it had evolved 5 c.c. of gas and then extracted with warm water. On re-heating, it was clearly indicated that the catalyst had been partly removed (curve 9).

(8) *Catalytic Action of Residue.*—The increase in velocity in the latter part of the decomposition, notwithstanding the decrease in the quantity of fulminate, points to the progressive formation of a catalyst. To confirm this, the residue from the fulminate in Fig. 3 was mixed with fresh fulminate and heated at 80°. This accelerated the decomposition, as shown in Fig. 4, in which curve No. 4 shows 1 gram of brown fulminate without admixture, and curve No. 1 shows 1 gram of the same fulminate with addition of 0·5 gram of residue.

(9) *Influence of Moisture.*—This retarded the decomposition very strongly, as shown by the following comparison.

Influence of Moisture.

Brown fulminate. Temperature 80°. Quantity 1 gram. Time of evolution in hours.

	1 c.c.	2 c.c.	3 c.c.	4 c.c.	5 c.c.
Fulminate alone	74	82	87	91	95
,, + 10 per cent. of water	188	228	245	255	263

The water may have caused the fulminate to pass to some extent into the more stable fulminurate.

(10) *Influence of Mercury Compounds.*—Metallic mercury and various mercury compounds were added to ascertain whether these affected the initial quiescent period or the subsequent velocity of decomposition, but these had only a slight influence. The type of curve remained unchanged, and the time of decomposition was not materially affected. For an evolution of 5 c.c. per gram the original brown fulminate required one hundred and twenty-two hours and the corresponding times for this fulminate with 10 per cent. of admixtures were as follows: Mercury (111), mercuric oxide (122·5), mercuric chloride (119), mercuric cyanide (116), mercurous chloride (110), mercurous oxalate (126).

(11) *Effect of other Admixtures.*—A range of admixtures was examined, in order to ascertain the types of compounds which accelerated or retarded the evolution of gas. The following table shows the results for admixtures of 10 per cent. of various substances (1 gram of brown fulminate, 0·1 gram of admixture) at 80°. Many of these fall so closely together that the admixtures may be said to be without effect on the stability.

Influence of Admixtures.

Brown fulminate. Quantity 1 gram. Temperature 80°. Time of evolution in hours.

	2 c.c.	5 c.c.		2 c.c.	5 c.c.
No admixture	104	122	Lithium carbonate	109·5	123·5
Magnesium powder	112·5	126·5	Magnesium carbonate	149	175
Tin	102·5	119	Calcium carbonate	112	124
Iron	102	120	Barium carbonate	100	116
Zinc	108·5	127·5	Lead carbonate	99	116
Copper	101·5	118	Lithium phosphate	126	140·5
Brass	100·5	117	Calcium stearate	133·5	158·5
Magnesium oxide	126	142·5	Acetanilide	104	123
Cupric oxide	103	119	Cetene	102	117
Zinc oxide	106	120·5	Nitric acid	detonated	
Lead oxide	99·5	116	Benzoic acid	104	—
Red lead	104·5	120	Potassium chlorate	99	113
Sodium carbonate	134	146	Potassium permanganate	105	—

In general, it appears that strong acid accelerates the decomposition; weak organic acids have no noticeable effect; alkalis retard somewhat. It has been noted earlier that water has a pronounced retarding influence; hence substances containing any trace of moisture are liable to delay the evolution of gas. Organic bases gave some rather curious effects, as shown in the following table.

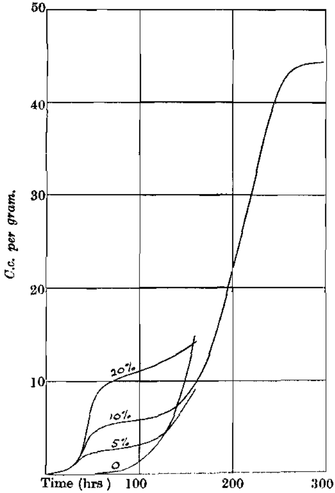
Influence of Nitrogen Bases.

	2 c.c.	4 c.c.	6 c.c.	8 c.c.	10 c.c.
Carbamide	1·5	3	6	30	168
Dicyanodiamide	133	145	153	160	166
Biuret	183	199	200	—	—
Carbazole	114	127	—	—	—
Phenazone	30	160	182	190	195

In one experiment, carbamide gave rise to an explosion after three hours from the start. Diphenylamine gave at first an accelerated evolution, followed by a remarkable decrease in the velocity, and then after a time the rate of evolution again increased. This was considered sufficiently noteworthy to call for experiments on different percentages of diphenylamine (Fig. 5). The total gas evolved on heating to complete decomposition was practically normal (44·5 c.c. per gram).

(12) *Influence of Subdivision.*—The degree of subdivision had a marked influence on the rate of decomposition on heating in a vacuum. In the case of brown fulminate, the type of the curve remained unchanged, but the initial quiescent period was considerably shortened. A similar effect was produced by compressing the fulminate into pellets, as the high pressure crushed the crystals to a fine powder.

FIG. 5.
Mixtures of fulminate with diphenylamine.



Influence of Grinding and Compression.

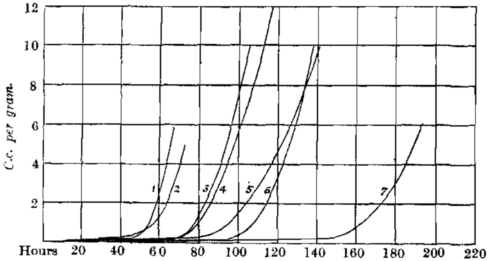
Temperature of test 80°. Quantity 1 gram. Time of evolution in hours.

	1 c.c.	2 c.c.	3 c.c.	4 c.c.	5 c.c.
Brown fulminate No. 20.					
Original	82	91	96	100	104
Ground under water and dried	71	75	78	81	84
Ground dry	54	63	67	70	73
Brown fulminate No. 24.					
Original	97	105	111	116	120
Ground dry	57	62	66	68	70
Compressed pellet (2 tons)	60	65	—	—	—
,, ,, (10 tons)	58	64	68	70	73
,, ,, (25 tons)	55	59	62	64	66
Brown fulminate No. 66.					
Original	74	82	87	91	95
Compressed pellet (2 tons)	71	79	83	86	88
,, ,, (20 tons)	45	53	56	58	59
,, ,,	50	58	61	63	65

The effect of subdivision on white fulminate is much more marked. The quiescent period is greatly reduced and the type of curve becomes almost identical with that of a brown fulminate, as shown in Fig. 6. Curve 7 shows an original white fulminate, curve 4 the same fulminate after grinding carefully in the dry state, curve 3 after grinding under water and drying, and curve 1 after compressing to a pellet. Curve 5 shows an original brown fulminate, and curve 2 the same compressed to a pellet. In some cases, white fulminate, as originally received, contained a very large proportion of dust, and in such cases gave decomposition curves approximating to those of brown fulminates. An example of this is curve 6 in Fig. 6, which shows a white fulminate (No. 59) which was in a very fine state of subdivision.

FIG. 6.

Influence of subdivision.



In one case a mixture of crystalline and finely powdered fulminate (white) was tested. In this case, the presence of the crystalline fulminate delayed the gas evolution from the finely powdered substance.

	No. of hours for an evolution of 0·5 c.c. at 80°.
Fine dust 0·0887 gram	110
Crystals 0·1043 gram	185
Mixture of these	148

The total evolution was approximately normal (44·5 c.c. per gram).

Influence of Light.

Brown and white fulminates were finely ground and exposed to daylight in the vacuum test apparatus. The light caused a slight

but distinct gas-evolution. This differed from the decomposition caused by heat, as it proceeded continuously from the start. When the apparatus was placed in the dark, the evolution ceased.

Decomposition of Mercuric Fulminate by Light.

Gas evolution from 3 grams of fulminate. Mean temperature 19°.

Hours	80	160	240	320	400	480
White fulminate No. 37 (c.c.)	0·11	0·23	0·30	0·37	—	—
Brown fulminate No. 20 (c.c.)	0·04	0·08	0·11	0·14	—	—
		continued in dark			0·14	0·14

Further samples were subjected to daylight for five weeks during the bright summer weather and then tested at 80°. The tests showed that the light had deteriorated the fulminates appreciably.

Vacuum Tests after Exposure to Light.

Temperature of test 80°. Quantity 1 gram. Time of evolution in hours.

	1 c.c.	2 c.c.	3 c.c.	4 c.c.	5 c.c.
Brown fulminate No. 24.					
Before exposure	95	104	111	117	122
After exposure	82	90	95	99	102
White fulminate No. 37					
Before exposure	162	173	180	185	189
After exposure	154	166	172	177	—

In a further series, the combined influence of light and moisture at the ordinary temperature was examined, the fulminates being tested at 80° in a vacuum after keeping.

Vacuum Test after Exposure to Light and Moisture.

Brown fulminates. Temperature 80°. Quantity 1 gram. Time in hours for the evolution of 2 c.c. of gas.

	Stored in dark.	Stored in light.
No. 52	111	105
No. 24	111	101

The thanks of the author are due to the Director of Artillery for permission to publish these results.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, November 28th, 1921.*]

XXIII.—*A Note on the Constitution of Benzene.*

By RONALD FRASER.

THE following is an attempt to apply the newer and more powerful stereochemical methods to the problem of the constitution of benzene.

Existing structural formulæ may be classified as static or dynamic; there appears, however, to be a considerable body of evidence converging on the conclusion that the electrons in the benzene molecule are arranged in a particularly stable configuration; that is, a static model is indicated, one in which no appreciable movement of the component parts of the molecule is possible.

A static formula receives strong support from the theory of Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762), who would attribute colour in compounds to weakly held electrons. On his view, since benzene is colourless, it can be postulated a priori that all electrons common to any two carbon atoms, or to a carbon atom and a hydrogen atom, are held firmly under definite forces.

Again, it is well known that there exists a close connexion between the dielectric constant (Walden, *Z. physikal. Chem.*, 1906, **54**, 129), the condition of saturation of the simple molecules, and the ionising power of a solvent. Those solvents which possess a high dielectric constant are just those which have great dissociating power, and which are themselves associated. The dielectric constant of benzene is very low, it is an associative, not a dissociative solvent. Its individual molecules are thus to be regarded as simple, a result also indicated by the Eötvös-Ramsay-Shields law. That is, their external field is small—a result in agreement with the low melting point of benzene. This means that the electrons in the molecule are arranged in a very stable, and therefore symmetrical configuration; that is, they are all firmly held under definite forces, as the colour theory of Lewis demands.

On these grounds, then, a static in preference to a dynamic model of the benzene molecule appears to be indicated.

A weakness common to many of the older structures proposed appears to lie in the fact that they are two-dimensional. It would seem very unlikely that the six carbon atoms of benzene are coplanar; and some sort of three-dimensional symmetry must therefore be postulated.

The most symmetrical structure possible would be one in which the six carbon nuclei are symmetrically disposed on the surface of a sphere, the centre of which is the centre of symmetry of the

molecule. That is, the carbon nuclei are located at the six corners of a regular octahedron.

It is clear, however, that such an arrangement cannot hold for the six hydrogen atoms, the positions of which determine those occupied by substituted groups. The behaviour of many *ortho*-derivatives (for example, phthalic acid) indicates clearly that two groups in the *ortho*-relation are decidedly nearer each other than two such groups in the *meta*-relation.

In point of fact, it has been found that by arranging the carbon nuclei in the most symmetrical way possible, at the same time having regard to the sharing of electrons between carbon atoms in accordance with Langmuir's theory of co-valence, the positions taken up by the hydrogen nuclei agree in every way with the considerations of the preceding paragraph.

Furthermore, it will appear in the sequel that there is a structural, and not merely spatial, distinction between the *ortho*-position and the *meta*-position.

It was thought that Langmuir's theory (*J. Amer. Chem. Soc.*, 1919, **41**, 868), in which a duplet (pair of electrons) held in common between two octets corresponds with the "bond" of the older theories, might prove successful in giving a definite picture of the benzene molecule.

In benzene we have six carbon atoms, each with four electrons in the sheath; and six hydrogen atoms, each with a single electron. There are thus thirty electrons available for the formation of octets. The number of octets formed is evidently six.

Substituting the appropriate values of n and e in the "co-valence equation," written

$$p = \tfrac{1}{2}(8n - e),$$

where p is the number of duplets held in common (that is, the number of bonds), n the number of octets formed, and e the number of electrons available for the formation of octets, we obtain $p = 9$.

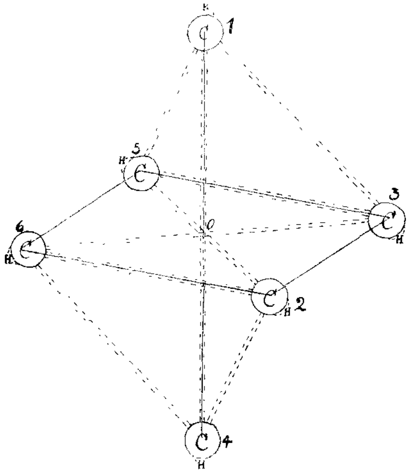
Nine duplets have therefore to be shared among the six carbon atoms arranged symmetrically in space.

Fig. 1 indicates the method of sharing proposed. Leaving out of account for the moment the actual configurations adopted by the electrons in the carbon octets, it will readily be seen that the mode of sharing duplets, indicated diagrammatically in the figure by dotted lines, is consistent with symmetry about the point O.

It will be seen that in each carbon octet one duplet is left free to hold the hydrogen nucleus. The six hydrogens are equivalent; for the condition, in relation to the molecule as a whole, of each carbon atom as regards sharing duplets with other carbon atoms is precisely similar.

The figure also shows that three, and no more than three, disubstitution isomerides are possible; for, if a group be already substituted in position 1, position 4 corresponds with the *para*-position, 2 and 6 are equivalent, and correspond with the *ortho*-positions, and the equivalent positions 3 and 5 with the *meta*-positions; and similarly if any other carbon atom is placed in position 1.

FIG. 1.



It might seem, from a study of Fig. 1 alone, that the positions there numbered 3 and 5 are in the *ortho*-relation to No. 1, and 2 and 6 in the *meta*-relation; not vice versa, as stated. As a matter of fact, the *kernels* of carbon atoms 3 and 5 are actually closer to that of 1 than are the kernels of 2 and 6, owing to the interpenetration of carbon sheaths sharing electrons in common. It will be clear later, from an examination of the space model I have constructed (Fig. 2), that, whilst this is so, the orientation of the carbon tetrahedra is such that the *hydrogen nucleus* attached to carbon atom 1 is actually nearer to the hydrogen nuclei attached to carbon atoms

2 and 6 than to those attached to 3 and 5. Thus 2 and 6 are to be regarded as *ortho* to No. 1, and 3 and 5 as *meta*.

Considering now *any one pair* of carbon octets sharing electrons, it is clear that one and only one duplet is held in common between the octets. This is a point of particular interest in view of the results obtained by Pease (*J. Amer. Chem. Soc.*, 1921, **43**, 991).

Pease has studied the volumes of isosteres, using as a means of comparison the value of the constant b occurring in the equation of van der Waals. The values of b * are calculated from the relation

$$b = \frac{1}{8}\frac{R\,T_c}{p_c},$$

where T_c, p_c are the critical temperature and pressure. The reader is directed to Pease's paper for references concerning the critical data used here.

Pease shows that there is a constant volume difference of 28 for the successive addition of a single hydrogen atom in H_2O (136), NH_3 (165), CH_4 (191). He takes this value as representing the volume occupied by hydrogen in combination. He finds that, expressed in terms of a single atom, the values of a single neon octet combined in various ways are: sharing no pairs (CH_4, etc.), 80; sharing one pair (C_2H_6), 59; sharing two pairs (O_2, C_2H_4), 72; sharing three pairs (N_2, C_2H_2), 87. These values refer to the sharing of duplets between *two* octets. He further suggests that the ratio 80/59 represents the relation between the cubic octet and the tetrahedral octet of neon.

Now the value of b for benzene is 537; subtracting 168 (28×6) from this, we get 369 as the value for the six carbon atoms. The value for a single carbon atom is thus 61·5. From this value it would appear that the carbon octet in benzene is of the tetrahedral type, in which the eight electrons are located in pairs at the four corners of a regular tetrahedron.

Further, on this view, *any one pair of carbon octets sharing electrons holds one and only one duplet in common between the octets.* This is precisely the result that follows the application of the co-valence equation, and indicates that there are no ethylenic linkings between carbon atoms in the benzene molecule.

The Space Model.

A model of the molecule according to the foregoing conclusions has been constructed, of which Fig. 2 is a photograph.

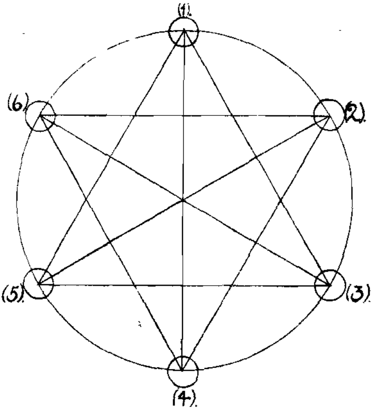
* The values of b used here are all $\times 10^5$.

A study of Fig. 2 shows:

(1) The six hydrogen atoms are equivalent (compare Fig. 1) the model will present precisely the same appearance no matter which tetrahedron is placed in position 1. This is brought out very clearly by the stereographic projection of the model (see Fig. 3) The hydrogen nuclei lie on the surface of a sphere concentric with that bearing the carbon nuclei.

(2) Three and only three disubstitution isomerides are possible (compare Fig. 1).

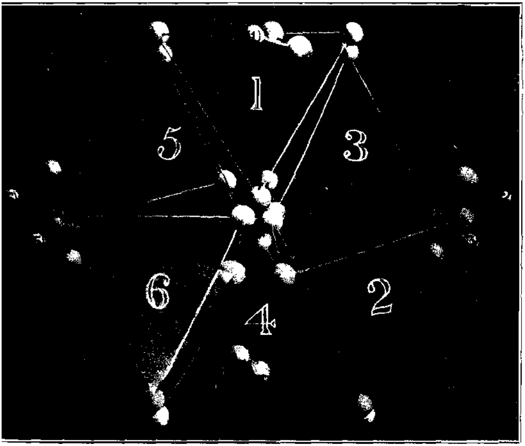
FIG. 3.



(3) There is a structural, and not merely spatial distinction between the *meta*- and *ortho*-positions; for whereas octets 3 and 5, which are in the *meta*-position to No. 1, share a duplet with No. 1, octets 2 and 6, which are in the *ortho*-position to No. 1, do not share a duplet with it.

(4) *Trisubstituted Derivatives.*—In considering a three-dimensional model, a new condition has been introduced with the third dimension. In a two-dimensional model, if the condition (2), that three and no more than three disubstitution isomerides are possible, is satisfied, the correct inter-relations of groups in a trisubstituted derivative follow automatically. This does not necessarily follow in a three-dimensional model, and the model illustrated in Fig. 2 has therefore

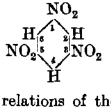
FIG. 2.



[To face Trans., p. 192

been tested for a large number of trisubstituted derivatives. It has been found in every case to give results in complete agreement with chemical behaviour.

If, for example, nitro-groups are introduced in positions (1), (3), and (5), giving trinitrobenzene,



it will be found that the relations of the unsubstituted hydrogen atoms among themselves, and to the nitro-groups agree perfectly with existing chemical theory. For example, hydrogen in position (2) will be found to be in the *meta*-position to the hydrogen atoms in positions (4) and (6), in the *para*-position to the nitro-group in position (5), and in the *ortho*-position to the nitro-groups in positions (1) and (3).*

(5) *Ethylenic Linkings.*—There are no ethylenic linkings in the model proposed, and on several grounds (vide supra) none is to be expected. Nevertheless, the structure proposed seems to indicate that the molecular refractivity should be of a magnitude corresponding with the presence of three ethylenic linkings. On the Langmuir co-valence theory, an ethylenic linking is represented by two tetrahedral octets joined along an edge. Considering, let us say, carbon octets 2 and 6, it is evident that this condition is fulfilled, except that the adjacent central electrons (indicated by cross hatching in Fig. 2) are *not* shared between octets 2 and 6, but between 2 and 5, and 6 and 3 respectively. The juxtaposition of the central electrons sharing with *opposite* carbon octets, would appear to confer half the value of a true ethylenic linking as between carbon octets 2 and 6. There are six such semi-ethylenic linkings in the proposed structure; hence one might be entitled to expect a value for the molecular refractivity indicating the presence of three true ethylenic linkings. The indication of ethylenic linkings given by the molecular refractivity has proved an insurmountable objection to all structures hitherto proposed in which each carbon atom is attached to three others; but the application of Langmuir's theory to the problem appears to remove, or at least materially to minimise, this difficulty.

* It is important to note that the model proposed leads to asymmetry among trisubstituted derivatives which ought to find expression in the occurrence of optical isomerism. Thus a derivative containing three dissimilar groups *X*, *Y*, and *Z*, ought to exist in *d*- and *l*- forms, if Fig. 2 is a correct representation of the benzene molecule. Although no benzene derivatives have as yet been isolated in optically active forms, this does not necessarily mean that they are incapable of being so isolated; and the author intends if possible to test this point experimentally.

(6) *Benzene Hexachloride*, $C_6H_6Cl_6$.—To this additive product, and of course to benzene hexabromide, is given a definite structure; it appears extremely probable that the six chlorine atoms are situated at the centroids of the equilateral triangles forming the bases of the carbon tetrahedra, being held there by the equal electrostatic attractions of the electrons which determine the triangles. One of these triangular bases is shown shaded in Fig. 2.

Stereographic Projection.—If a projection be made, on the horizontal great circle, of the space model placed as in Fig. 2, a regular star-shaped form will be obtained (Fig. 3). The numbered circles represent hydrogen nuclei, and the lines joining them the manner in which the hydrogen nuclei are inter-connected—via the carbon octets holding them. It has been noted already that it is the positions of the hydrogen nuclei, and only indirectly those of the carbon nuclei, which determine the positions adopted by entering groups. It will be observed that Fig. 3 corresponds exactly with the modified form of Ladenburg's original projection formula ("Theorie der aromatischen Verbindungen," Brunswick, 1876), except that the points of the star are occupied by hydrogen nuclei, and *not* by carbon atoms.

Some interesting results follow the application of the present theory to the differences in the melting points of disubstitution isomerides, and to the Crum-Brown rule. These will now be considered.

The tetrahedral arrangement of the electrons in the sheath of the carbon atom is apparently a somewhat unusual one; the commonest type of configuration for neon and argon isosteres would seem to be the cube.

Now, when any of the hydrogen atoms of benzene is replaced by a cubic octet, or by a group the kernel octet of which is cubic, the pair of electrons at the hydrogen corner of the corresponding carbon tetrahedron will be drawn apart slightly, disclosing the kernel of the carbon atom. This will give rise to a small external field.

Suppose a group substituted for hydrogen in position (1) (see Fig. 2); if a second group be introduced, the molecule will exhibit polarity, due to the two positively charged carbon kernels thereby exposed. If the second group enter the *ortho*-position *or* the *meta*-position, the two positive charges will be asymmetrically disposed; in the *para*-position, however, the two positive charges are symmetrically placed on a molecular axis.

Owing to the more perfect symmetry of the stray field, the stability of a molecular system would appear to be greater in the case of the *para*-form than in the case of the *ortho*- or *meta*-form; hence it is to be expected that *para*-substituted di-derivatives *should exhibit a higher melting point than the corresponding* ortho- *or* meta-*isomerides.*

The stabilities of two molecular systems, one composed of the *ortho*-form, the other of the *meta*-form, would appear to be very similar; for the two positively charged carbon kernels are similarly situated in the two cases. Nevertheless, a difference in the melting points is to be looked for. Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543) concludes that the melting point is peculiarly sensitive to even small changes in structure; and, as has already been noted, there is a structural distinction between the *meta*- and the *ortho*-positions, inasmuch as carbon octets 3 and 5 share a duplet with 1, whereas 2 and 6 do not.

The difficulty experienced in separating the xylenes may possibly be due to the tetrahedral character of the carbon octet in the methyl group, whereby little or no external field is developed.

Owing to the symmetrical disposition of the positive charges in the *para*-substituted isomerides, one would expect the molecules in the liquid state to exhibit a tendency to set themselves out in chains, rings, or other definite formation. It has been estimated that in a quantity of matter there are about as many free electrons present as there are molecules. Hence a possible structure for these chains would be one in which a molecule and an electron alternated; thus:

$$+\bigcirc+\ \bar{\epsilon}\ +\bigcirc+\ \bar{\epsilon}\ +\bigcirc+\ \bar{\epsilon}\ +\bigcirc+$$

Such a stable, definite orientation of the molecules might be expected to lead to the formation of *liquid crystals*. On these grounds, since no such stable chain is possible with the asymmetrically charged *meta*- and *ortho*-forms, it is to be expected that *para*-isomerides would show this property to an enormously greater extent. The substances listed by Vorländer (*Ber.*, 1906, **39**, 803; 1907, **40**, 1415) bear out this deduction in a remarkable manner.

The Rule of Constancy of Substitution-type.

It is well known that a second substituent is directed into the *para*-position or the *ortho*-position by the presence of: the halogens, and the groups OH, NH_2, CH_3; but into the *meta*-position by the groups SO_3H, CO_2H, NO_2, and CN.

It is evident that the groups which substitute in the *para*- and *ortho*-positions contain a single octet or equivalent stable configuration. The groups substituting in the *meta*-position contain two or three octets. That is, the groups of *small volume* substitute in the *para*- and *ortho*-positions, the groups of *large volume* in the *meta*-position.

Suppose a group already substituted in position (1). A second

similar group entering the molecule will tend, *ceteris paribus*, to go to the *para*-position, as being the most stable and symmetrical arrangement possible. But an upper limit is set to the volume of the entering group by the strength of the bond between carbon octets 1 and 4; hence, if above a certain volume, the group will not readily enter the *para*-position.

If the entering group approach closely to carbon octet No. 1, it will be attracted to it by the exposed kernel, and will tend to go to the *ortho*-position. The angle subtended at the centre by positions (1) and (2) or (6) is 60°; by positions (1) and (3) or (5), 120°. Now, *two* groups (the group already introduced, and the entering group), will have to find room, preferably between positions (1) and (2) or (6), or else between (1) and (3) and (5); but (see Fig. 2) there is less room for them in the former case than in the latter. Hence if the groups are above a certain volume, the entering group will not readily adopt the *ortho*-position.

Substituents of small volume, therefore, would be expected to substitute in the *para*- and *ortho*-positions for preference, substituents of large volume in the *meta*-position. It is not claimed that volume is the only factor, but it appears beyond doubt that volume considerations are of importance in determining the type of substitution possible under given conditions.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF ABERDEEN. [*Received, December 6th*, 1921.]

XXIV.—*The Autoracemisation of Potassium Chromioxalate.*

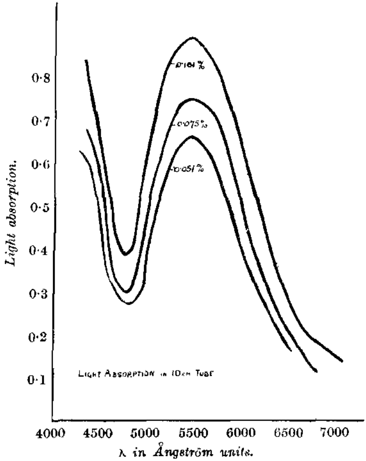
By ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS.

IN the course of his investigations on the optically active inorganic complex salts of chromium, Werner found that the active forms of potassium chromioxalate underwent rapid racemisation in aqueous solution. His data (*Ber.*, 1912, **45**, 3061) indicate that an aqueous solution of this salt possesses negligible activity after a period of less than one hour and a half at room temperature. The instability of these active salts has likewise been confirmed by Jaeger (*Rec. trav. chim.*, 1919, **38**, 171). The velocity coefficient of autoracemisation due to intramolecular change has generally a large temperature coefficient, as is exemplified by the work of Mills and Bain on salts of both *d*-oximino*cyclo*hexane-4-carboxylic acid (this

Journal, 1877, **31**, 1910) and *cyclo*hexanone-4-carboxylic acid benzoylphenylhydrazone.

It was deemed of interest to investigate whether the inorganic complex salts, of which potassium chromioxalate is one of the most suitable for examination, possess a similar high velocity-temperature coefficient and in addition whether the velocity of reaction is affected by a change in the environment of the salt.

FIG. 1.



Experimental.

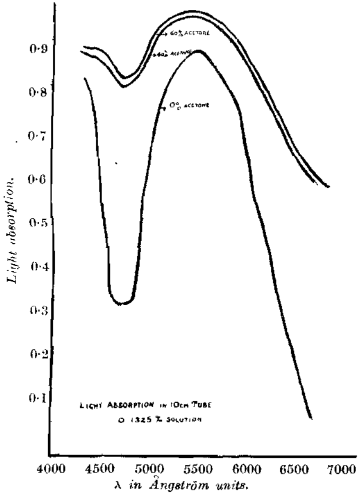
The racemic salt was prepared by Croft's method, that is, a solution of potassium dichromate was heated with the necessary amounts of potassium oxalate and oxalic acid. The complex salt was then precipitated from aqueous solution by the addition of three times its volume of 97 per cent. alcohol. The resolution was carried out by crystallisation of the potassium distrychnine salt (Werner, *Ber.*, 1912, **45**, 3061) and this converted into the tripotassium salt by means of potassium iodide.

Dilute aqueous solutions of the salt were prepared and these were

found to undergo rapid racemisation at room temperature. In general, a small amount of insoluble residue was left on solution of the salt in water; consequently, the dilute solution was poured off from the apparently insoluble residue and the concentration determined from the absorption spectra, the value thus obtained being confirmed by extrapolation of the specific rotation to zero time.

In the following curves are given the data on the light absorption of dilute solutions of the salt in water over a range of $\lambda = 4000$ Å.U.

Fig. 2.



to $\lambda = 7000$ Å.U., the values of the absorption for various wavelengths being determined in a decimetre tube by means of a Nutting spectrophotometer.

It will be noted that within the range examined the salt possesses strong general absorption within the region $\lambda = 4000$ to 4250 and a marked absorption band at $\lambda = 5500$ to 6000 Å.U.

For the determination of the rate of decay of the optical activity, a Hantzsch-Schmidt polarimeter was employed, utilising the prominent line $\lambda = 5461$ Å.U. of a quartz mercury vapour lamp as a

source of illumination. Portions of dilute solutions maintained in a thermostat at the required temperature were removed from time to time and placed in a decimetre polarimeter tube also maintained at the same temperature. The time of measurement of each of the duplicate readings on the polarimeter could with a little practice be reduced to less than thirty seconds.

The values thus obtained for the rotation were plotted as functions of the time, the velocity coefficients for five-minute intervals being calculated therefrom according to the general expression for a unimolecular reaction

$$-\frac{dc}{dt} = K(a - c).$$

In the following tables are given the values of the observed angles of rotation and the velocity constant K for different time intervals (The values of K are calculated to the natural base e with the second as unit of time). In spite of the smallness of the angle observed, a limitation imposed by the deep colour of the solution, the values for the constants calculated for a unimolecular reaction are sufficiently concordant to indicate that the racemisation follows this course.

Temp.	0°.		11°.		22°.		24°.	
Conc. in mole per litre.	0·00144.		0·00130.		0·00143.		0·00107.	
Time in min.	a*.	$K \times 10^5$.	a*.	$K \times 10^5$.	a*.	$K \times 10^5$.	a*.	$K \times 10^5$.
5	54·3		46·0		47·2		35·0	
		15·0		30·1		59·7		60·8
10	51·8		42·0		39·5		29·1	
		16·1		28·8		50·0		58·0
15	49·3		38·5		34·0		24·5	
		16·1		30·9		50·0		58·0
20	46·8		35·1		29·6		20·5	
		15·7		30·1		45·4		55·3
25	44·6		32·0		26·3		17·3	
		13·8		29·2		45·4		58·0
30	42·8		29·2		23·0		14·5	
		14·5		28·3		53·0		58·3
35	41·0		26·7		20·0		12·2	
		15·0		29·0		53·9		55·3
40	39·2		24·5		17·0		10·3	
		14·5		30·1		57·8		67·4
45	36·0		20·5		12·0		6·9	
		14·6		29·7		63·3		67·3
50	33·0		17·1		8·2		4·6	
		13·5		29·7		63·4		
70	30·5		14·3		5·6			
		15·1		26·3				
80	28·4		12·3					
		15·0						
90	26·3							
		15·5						
100	24·0							

* The values of a are given in hundredths of a degree.

Mean value of K, 0·000149, 0·000293, 0·000542, 0·000598.

Extrapolating to zero time at 0°, we find $\alpha = 0{\cdot}562°$, whence

$$[\alpha] = \frac{100\,\alpha}{l \times c} = 1094°, \text{ and } [M] = \frac{M\,[\alpha]}{100} = 4760°.$$

It will be noted that the temperature coefficient is relatively small, being approximately 1·75 for a rise of 10°, equivalent to an energy of activation of 9650 cals. per mole and an intramolecular vibration frequency of $1{\cdot}031 \times 10^{14}$ (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226; Haber, *Ber.*, 1880, **13**, 1117, 1911).

The low temperature coefficient indicates the probability that the reaction involves the solvent and is only pseudo-unimolecular. This is confirmed by the fact that the dry salt can be heated at 90° without undergoing racemisation, and that, as Werner indicated, addition of acetone to the solvent greatly decreases the rate of autoracemisation.

The influence of acetone on the velocity constants is very marked, as is observable from the following experimental data.

Temp. 22·0°	Acetone per cent.	Moles of acetone per litre.	Moles of water per litre.	K.
	0	0	55·55	0·000542
	40	5·49	33·33	0·000329
	60	8·23	22·22	0·000262

The diminution in velocity may be ascribed to a change in the thermodynamic environment of the salt, and with Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173) we may express the reaction velocity as a function of the molar concentrations and the specific catalytic effect of each constituent in an exponential form,

$$K = K_0\, e^{aw + bv},$$

where a is the specific catalytic effect of the water of concentration w, b, and v are the corresponding values for acetone, and K_0 is the reaction velocity in an inactive environment.

Inserting the above values we obtain

$$0{\cdot}000542 = K_0 e^{55{\cdot}55\,a}$$
$$0{\cdot}000329 = K_0 e^{33{\cdot}33\,a + 5{\cdot}49b}$$
$$0{\cdot}000262 = K_0 e^{22{\cdot}22\,a + 8{\cdot}23b}.$$

In pure acetone, the salt is entirely insoluble, and presumably this salt exerts no specific catalytic action. Equating $b = 0$, we obtain for a the values 0·0205, 0·0225, and 0·0219, giving a mean value of $a = 0{\cdot}0216$ for the specific catalytic effect of the water. Likewise, for K_0, the reaction velocity in an environment which exerts no specific catalytic effect, we obtain a mean value of $K = 0{\cdot}000158$.

The function of the acetone in reducing the reaction velocity is thus one of replacement of an active solvent by an inactive one.

Not only does the velocity coefficient of autoracemisation alter on the addition of acetone, but there occur simultaneously a decrease in the electrolytic conductivity of the solution and a marked change in the absorption spectrum.

The alteration in the absorption spectrum on the addition of acetone is depicted in Fig. 2.

The conductivity of the various solutions was determined at 25° by the method of Kohlrausch. The following values were obtained:

Aqueous Solution.

Salt content per cent.	Molecular conductivity.
0·1028	346
0·0514	368
0·0257	402
0·0206	433
0·0041	697
0·0000	820 by extrapolation.

The molecular conductivity calculated from the ionic conductivities of the potassium, chromium, and oxalate ions is 757. The above value of 820 for the molecular conductivity is also far in excess of the value for other quaternary electrolytes. Thus the salt in dilute solutions dissociates entirely into the ions $3K^{\cdot}$, $Cr^{\cdot\cdot\cdot}$, and $3C_2O_4{}''$.

In aqueous acetone, the molecular conductivities were found to be:

Salt conc. per cent.	40 per cent. acetone.	60 per cent. acetone.
0·1028	183	132
0·0514	194	151
0·0257	—	179

The supposition that autoracemisation in the case of the inorganic complex salts is due to ionisation (see Thomas, T., 1921, **119**, 1140) is also supported by the fact that the complex oxalates of iron, chromium, and cobalt react with dilute silver nitrate with the formation of silver oxalate. The ferri-complex, which racemises with great rapidity, gives immediately a dense, white precipitate. The chromi-salt produces a precipitate on keeping.

Summary.

The absorption curve and the rate of autoracemisation of potassium chromioxalate have been determined at various temperatures; the temperature coefficient was found to be approximately 1·75 for a 10° rise, and the critical energy increment 9650 cal. per

gram-molecule. The absorption spectrum in water shows selective absorption within the region λ 4000—4250 Å.U., and a band at λ 5500—6000 Å.U. In acetone, the rate of autoracemisation is very much decreased. The change in velocity is apparently connected with the ionisation in solution, and is accompanied by changes both in the specific conductivity and in the absorption spectrum.

University Chemical Laboratories,
Cambridge. [*Received, November 30th, 1921.*]

XXV.—*Preparation and Properties of the Benzochloroamides.*

By George Robert Elliott.

The author found that the action of ammonium hydroxide on benzomonochloroamide gives an almost quantitative yield of phenylcarbamide; as benzoylhydrazine, which might have been formed, does not undergo intramolecular change to phenylcarbamide, the formation of the latter requires some other explanation.

Several related anomalies have been recorded. Blacher (*Ber.*, 1895, **28**, 435), by the action of iodine on sodium benzamide, obtained benzoylphenylcarbamide instead of the substituted hydrazine expected. Titherley (T., 1901, **79**, 391) obtained an alkylacylcarbamide by the action of a sodamide on a bromoamide. Folin (*Amer. Chem. J.*, 1897, **19**, 323) and Swartz (*ibid.*, 1897, **19**, 319), by the reaction of substituted bromoamides with sodium ethoxide, obtained substituted urethanes, and not hydroxylamine derivatives.

Each of these results seems to indicate the intermediate formation of a carbimide; and up to this stage, all the reactions are probably identical with that of Hofmann for the preparation of amines from halogenoamides, which, according to Graebe and Rostovzeff (*Ber.*, 1902, **35**, 2747), passes through the following phases, where X represents a halogen atom:

$$R{\cdot}CO{\cdot}NHX + NaOH \longrightarrow R{\cdot}CO{\cdot}NNaX \longrightarrow R{\cdot}NNa{\cdot}COX \longrightarrow R{\cdot}N{:}CO + NaX.$$

$$R{\cdot}N{:}CO + H_2O \longrightarrow R{\cdot}NH{\cdot}CO_2H \longrightarrow R{\cdot}NH_2 + CO_2.$$

In the cases cited, however, it would seem that the stages subsequent to the formation of the substituted carbimide become modified; thus, with benzochloroamide and ammonium hydroxide,

$$R{\cdot}N{:}CO + NH_3 \longrightarrow R{\cdot}NH{\cdot}CO{\cdot}NH_2;$$

with iodine and the sodamide,

$$R\cdot N{:}CO + R\cdot CO\cdot NHNa \longrightarrow R\cdot NH\cdot CO\cdot NNa\cdot COR$$
$$R\cdot NH\cdot CO\cdot NNa\cdot COR + H_2O \longrightarrow R\cdot NH\cdot CO\cdot NH\cdot COR + NaOH;$$

and with sodium ethoxide and a bromoamide,

$$R\cdot N{:}CO + EtOH \longrightarrow R\cdot NH\cdot CO_2Et.$$

As phenylcarbimide is probably an intermediate product in all these reactions, and as it also appears to be easily formed from benzomonochloroamide, the study of the latter appeared to be of interest. Whilst attempting its preparation by the action of bleaching powder and acetic acid on benzamide (Bender, *Ber.*, 1886, **19**, 2274), the author found that when the amide was dissolved in moderately concentrated instead of in dilute acetic acid, the product was a heavy, yellow oil which appeared to be *benzodichloroamide*, $C_6H_5\cdot CO\cdot NCl_2$; as this compound does not appear to have been described, some of its reactions were examined.

The investigation of benzomonochloroamide showed that in all its reactions with alkalis the chloroamide is first converted into phenylcarbimide, which then condenses with a suitable compound present. Experiment has further shown that benzomonochloroamide can, in many cases, be employed as a source of phenylcarbimide prepared in situ; being easily obtainable and capable of being stored without deterioration, the monochloroamide may bring to more general use the great reactivity of the carbimide.

EXPERIMENTAL.

Preparation of Benzomonochloroamide and of Benzodichloroamide.

Datta and Ghosh (*J. Amer. Chem. Soc.*, 1913, **35**, 1044) prepared benzomonochloroamide by chlorination for about four hours, of an aqueous suspension of benzamide, until the suspended solid had the desired melting point. Working with an aqueous or acetic acid solution, the author obtained a crystalline precipitate of the monochloroamide, which on further chlorination changed into a heavy, yellow oil, which proved to be the *dichloroamide*, $C_6H_5\cdot CO\cdot NCl_2$. With a more rapid stream of chlorine, the intermediate monochloroamide did not appear. The action of hydrochloric acid on the oil gave the monochloroamide with evolution of chlorine; consequently, the latter compound only is obtained by chlorination of a hydrochloric acid solution of benzamide. Good results were obtained with a saturated solution in approximately $3N$-acid; the monochloroamide separated almost immediately, and the time required for complete chlorination of 10 grams of benzamide was

about forty-five minutes. The benzomonochloroamide thus obtained was almost pure, and after recrystallisation from hot water melted at 117°. The yield was 90 per cent. of the theoretical, exclusive of the material remaining in the mother-liquid. The advantage of this method of preparation is that a well-defined product is obtained automatically, and its purity is independent of the exact duration of the passage of chlorine.

Reactions of Benzomonochloroamide.

The action of sodium hydroxide and of sodium carbonate on benzomonochloroamide has been elucidated by Hofmann (*Ber.*, 1882, **15**, 756), Graebe and Rostovzeff (*loc. cit.*), and Mohr (*J. pr. Chem.*, 1905 [ii], **71**, 133 ; **72**, 297) with reference to the formation of aniline, diphenylcarbamide, and benzoylphenylcarbamide.

The conditions for the preparation of the latter two substances are difficult to define, as the temperature, and more especially the concentrations of alkali and chloroamide, determine the nature of the final product.

According to the author's observations, the formation of diphenylcarbamide requires a dilute solution of the chloroamide (at the most 2 grams per 100 c.c. of total solution) and *N*/5-sodium hydroxide solution ; whilst benzoylphenylcarbamide requires a more concentrated solution of the chloroamide (at least 2 grams per 40 c.c. of total solution) and *N*/2-sodium hydroxide solution.

The results of a few experiments at the ordinary temperature are appended :

Conc. of alkali.	2*N*.	2*N*.	0·6*N*.	0·2*N*.
C.c. of solution per gram of chloroamide	6	60	20	60
Result with NaOH.	Benzoylphenylcarbamide.	Diphenylcarbamide and traces of aniline.	Benzoylphenylcarbamide.	Diphenylcarbamide and traces of aniline.
Result with Na_2CO_3.	,,	—	,,	Benzoylphenylcarbamide.

In each case the substituted carbamide separated in needles, the reaction being slower in the case of diphenylcarbamide than in that of benzoylphenylcarbamide, which was produced within a few minutes. The yields were almost theoretical.

Phenylcarbimide is formed in each case, the divergence being in its subsequent reactions. The transformation into aniline (compare Hofmann's reaction) will affect only a part of the phenylcarbimide

if less concentrated alkali be used, and the aniline formed will then react with the remainder to give diphenylcarbamide. In the formation of benzoylphenylcarbamide the phenylcarbimide does not reach the aniline stage, but, according to Stieglitz and Earle (*Amer. Chem. J.*, 1908, **30**, 412), reacts with unchanged benzomonochloroamide thus:

$$C_6H_5\cdot CO\cdot NHCl + C_6H_5\cdot N{:}CO = C_6H_5\cdot CO\cdot NCl\cdot CO\cdot NH\cdot C_6H_5.$$

$$C_6H_5\cdot CO\cdot NCl\cdot CO\cdot NH\cdot C_6H_5 + NaOH = C_6H_5\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_5 + NaOCl.$$

Benzomonochloroamide dissolves readily in ammonium hydroxide solution with development of heat, and on cooling, colourless needles of phenylcarbamide separate; these, after recrystallisation from water, melt at 147°. A 90 per cent. yield of the pure substance (m. p. 147°) is obtained after the mother-liquor has been evaporated.

As ammonium hydroxide no doubt first reacts as an alkali to give phenylcarbimide, a stream of dry ammonia was next passed into a warm benzene solution of the chloroamide. This caused the immediate separation of colourless needles (m. p. about 106° with loss of ammonia), which could not be recrystallised from warm solvents owing to decomposition into ammonia and benzomonochloroamide. This product was the ammonium salt of the chloroamide, $C_6H_5\cdot CO\cdot NCl\cdot NH_4$; it dissolved completely in cold water, but after some time a white precipitate separated. At room temperature the precipitation required several hours for completion, but at higher temperatures the product was dark in colour. The aqueous solution contained ammonium chloride and was acid to litmus; during the reaction, carbon dioxide was formed, and the presence of a little aniline indicated the intermediate formation of phenylcarbimide. After several recrystallisations from benzene, the precipitate melted at 208° (Found: N = 16·65 per cent.); it was hydrolysed by sodium hydroxide solution giving ammonia, aniline, and carbon dioxide, but no benzoic acid.

These facts show the compound to be *s*-diphenylbiuret, $NH(CO\cdot NHPh)_2$ (m. p. 208—210°. Calc., N = 16·45 per cent.).

The above reaction is not influenced by the presence of a large excess of ammonium chloride, and therefore the intermediate formation of phenylcarbamide from phenylcarbimide and ionised ammonium chloride is improbable, since excess of the latter would then give phenylcarbamide as the final product.

The reactions which occur are possibly those indicated below:

$$C_6H_5\cdot CO\cdot NCl\cdot NH_4 \longrightarrow C_6H_5\cdot N{:}CO + NH_4Cl.$$

$$C_6H_5\cdot CO\cdot NCl\cdot NH_4 + C_6H_5\cdot N{:}CO \longrightarrow C_6H_5\cdot CO\cdot NCl\cdot NH_3\cdot CO\cdot NH\cdot C_6H_5.$$

The product, undergoing the usual Beckmann transformation, may give the biuret with or without fission to, and subsequent condensation of, phenylcarbimide and phenylcarbamide hydrochloride :

$$\underset{\text{ClN}}{C_6H_5\cdot\overset{\|}{C}\cdot O\cdot NH_3\cdot CO\cdot NH\cdot C_6H_5} \longrightarrow \underset{C_6H_5\cdot N}{Cl\cdot\overset{\|}{C}\cdot O\cdot NH_3\cdot CO\cdot NH\cdot C_6H_5}$$

$$\longrightarrow C_6H_5\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_5 + HCl.$$

Swartz (*loc. cit.*) found that sodium ethoxide in alcoholic solution reacts with benzobromoamide to give a mixture of benzamide, phenylurethane, and benzoylphenylcarbamide, the principal reaction in concentrated solution being reduction of the bromoamide, and, in dilute solution, the formation of the urethane.

The author's experiments show that this reaction is slightly modified in the case of benzochloroamide owing to its greater stability. No reduction to benzamide was discovered, and the nature of the product was determined, not by the concentration, but by the amount of alkali used.

Experiment I.—When equivalent quantities of sodium ethoxide and the chloroamide were employed, sodium chloride separated and phenylurethane remained in solution.

Experiment II.—When two equivalents of sodium ethoxide were employed, sodium chloride separated first, and then a magma of needles consisting of the sodium compound of phenylurethane, $C_6H_5\cdot NNa\cdot CO_2Et$ (phenylurethane separated immediately on addition of water to this compound).

Experiment III.—With half an equivalent of sodium ethoxide, benzoylphenylcarbamide was obtained, the phenylcarbimide having condensed with unchanged benzochloroamide even in presence of excess of alcohol.

By adding sodium hydroxide solution drop by drop to a mixture of the chloroamide and a slight excess of phenol suspended in a little water, with constant shaking in the cold, a magma of needle-shaped crystals was obtained; this compound, on recrystallisation from benzene, melted at 126°, and proved to be phenyl phenylcarbamate, $C_6H_5\cdot NH\cdot CO\cdot O\cdot C_6H_5$.

An attempt to prepare the hydrazine, $C_6H_4{<}^{CO}_{CO}{>}N\cdot NH\cdot CO\cdot C_6H_5$, was made by treating the chloroamide with potassium phthalimide in alcoholic solution; but the precipitate which was rapidly formed crystallised from alcohol in colourless needles melting at 140°, and proved to be ***phthalylphenylcarbamide***, $C_6H_4{<}^{CO}_{CO}{>}N\cdot CO\cdot NH\cdot C_6H_5$, which has not previously been described.

The action on the chloroamide of ethyl sodiomalonate suspended in benzene was examined in order to discover if the phenylcarbimide produced would react with the enolic form of ethyl malonate; but even in absence of sodium ethoxide, benzoylphenylcarbamide was obtained. The reaction was evidently:

$$\mathrm{CH}\begin{cases}\mathrm{CO_2Et}\\ \mathrm{C}{<}^{\mathrm{OEt}}_{\mathrm{ONa}}\end{cases} + \mathrm{C_6H_5{\cdot}CO{\cdot}NHCl} \longrightarrow \mathrm{CH_2}\begin{cases}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{cases} + \mathrm{C_6H_5{\cdot}CO{\cdot}N}{<}^{\mathrm{Na}}_{\mathrm{Cl}},$$

and the phenylcarbimide then formed through the usual series of *reactions, combined with unchanged chloroamide.*

Equivalent quantities of sodium and benzochloroamide were heated together under reflux for two hours in dry benzene solution. Sodium chloride separated, aud on cooling, benzoylphenylcarbamide was deposited; no evidence of the presence of a hydrazine was obtained. As no alkali was present, the equations for the formatiou of benzoylphenylcarbamide by the action of sodium hydroxide require modification; and to conform with the facts discovered by Stieglitz and Earle (*loc. cit.*), that phenylcarbimide will not condense with acid amides, although it does so readily with acid halogeno-amides, the simplest representation of the reaction seems to be:

$$\mathrm{C_6H_5{\cdot}CO{\cdot}NHCl + Na \longrightarrow C_6H_5{\cdot}CO{\cdot}NNaCl + H \longrightarrow C_6H_5{\cdot}N{:}CO + NaCl + H.}$$

$$\mathrm{C_6H_5{\cdot}CO{\cdot}NHCl + C_6H_5{\cdot}N{:}CO \longrightarrow C_6H_5{\cdot}CO{\cdot}NCl{\cdot}CO{\cdot}NH{\cdot}C_6H_5.}$$

$$\mathrm{C_6H_5{\cdot}CO{\cdot}NCl{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + H_2 \longrightarrow C_6H_5{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + HCl.}$$

Benzochloroamide was heated under reflux with excess of dry benzene in the presence of anhydrous aluminium chloride for several hours, in an attempt to obtain benzanilide. Hydrogen chloride was evolved, but the main product proved to be benzamide; in absence of aluminium chloride, the chloroamide remained unchanged.

The main product of the action of aniline on benzochloroamide proved to be benzanilide, and no substituted hydrazine was formed. When dimethylaniline was employed, the mixture passed through shades of green and blue, to give, finally, a violet solution which, on cooling, deposited crystals. This compound, purified by distillation, proved to be benzamide. The violet coloration was due to the formation of traces of methyl-violet, which according to Brunner and Brandenburg (*Ber.*, 1877, **11**, 697), is produced by the action of bromine on dimethylaniline.

The Use of Benzochloroamide as a Substitute for Phenylcarbimide.

The experiments on the action of sodium ethoxide and of sodium phenoxide on benzochloroamide have indicated the procedure necessary to bring about the condensation of the phenylcarbimide formed, with a compound containing an alcoholic or a phenolic hydroxyl group. The preferential condensation of the phenylcarbimide with excess of the chloroamide in presence of alcohol further indicated that alcohol could be used as an indifferent solvent, and sodium ethoxide as alkali, provided that the compound with which it was desired to bring about condensation were an amiuo-compound present in slight excess.

In an attempt to prepare phenyl-*p*-tolylcarbamide from *p*-toluidine and benzochloroamide, the use of sodium hydroxide with an aqueous or dilute alcoholic solution of the mixed compounds was unsuccessful; but by dissolving the mixture in alcohol and then adding an alcoholic solution of sodium ethoxide, a crystalline mass was obtained which proved to be phenyl-*p*-tolylcarbamide (m. p. 212°).

Combination with aniline was found to take place in aqueous solution. Thus diphenylcarbamide was most simply prepared by warming a dilute sodium hydroxide solution of the chloroamide in presence of an equivalent quantity of aniline; the yield was almost quantitative.

These results seem to indicate that although preliminary experiment is necessary to ascertain the best conditions for the condensation to take place, benzomonochloroamide can be used, in many cases, as a source of phenylcarbimide prepared in situ.

Reactions of Benzodichloroamide, $C_6H_5\cdot CO\cdot NCl_2$.

This compound, which is a heavy, yellow oil, proved to be very unstable, and on exposure to air for several days lost chlorine continuously, giving benzomonochloroamide. It readily converted benzamide or acetamide to the monochloroamide. With hydrochloric acid and with sulphurous acid it gave the monochloroamide, a vigorous evolution of chlorine taking place in the former case. It gradually dissolved, apparently unchanged, in concentrated sulphuric acid, but on dilution with water, chlorine was evolved and the monochloroamide separated.

The dichloroamide dissolved in cold sodium carbonate solution, slowly and with evolution of carbon dioxide and nitrogen. On acidifying the solution, a precipitate of benzoic acid was obtained. On boiling the sodium carbonate solution with sodium hydroxide,

no aniline was formed; the possibility of the formation of sodiobenzochloroamide as an intermediate compound was thus excluded, since Hofmann's reaction would then have progressed. The oil dissolved much more quickly in dilute sodium hydroxide solution, with development of heat and evolution of nitrogen. In the early stages of the reaction an odour of benzonitrile was noticeable, but this was soon masked by an overwhelming odour of the carbylamine. A little aniline was obtained by distilling the alkaline solution in steam, indicating the formation of phenylcarbimide at some stage. By acidifying, benzoic acid was obtained at all stages, even before the odour of the carbylamine became evident.

Assuming the oil to be benzodichloroamide, its action with alkalis is readily explained. Displacement of chlorine atoms by hydroxyl groups probably first occurs, and the unstable compound $C_6H_5{\cdot}CO{\cdot}N(OH)_2$ can then decompose in the three ways yielding

(1) $C_6H_5{\cdot}CN + O_2 + H_2O$, (2) $C_6H_5{\cdot}NC + O_2 + H_2O$, and
(3) $C_6H_5{\cdot}N{:}CO + O + H_2O$,

the phenylcarbimide in (3) being formed either directly or by oxidation of the carbylamine. The reaction with sodium carbonate solution appears to be confined to reaction (1); but sodium hydroxide solution gives all three products. The formation of nitrogen is explained by the oxidation of the ammonia liberated in the hydrolysis of benzonitrile to benzoic acid.

The action of ammonium hydroxide on the oil gave phenylcarbamide with development of heat; the formation of nitrogen trichloride, indicated by a flash in the tube, confirmed the preliminary reduction of the dichloroamide to the monochloroamide requisite for the production of the phenylcarbamide.

The evidence of a chlorine estimation cannot be taken as conclusive evidence of the chlorine content of the oil, owing to the continuous loss of chlorine making impossible the choice of a sample free from dissolved chlorine, yet undecomposed. A sample which had been exposed to the air for two days gave Cl = 35 per cent. (Calc., Cl = 37·3 per cent.).

In oonclusion, the author wishes to express his indebtedness to Professor F. S. Kipping, F.R.S., for his interest in this work.

THE CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, June 23rd,* 1921.]

XXVI.—*The Oxidising Properties of Sulphur Dioxide. Part III. Copper Chlorides.*

By William Wardlaw and Frederic William Pinkard.

The present communication is an account of experiments made with the object of extending our knowledge of the oxidising properties of sulphur dioxide. The earlier work on the subject is detailed in *Proc. Durham Phil. Soc.*, 1914, **5**, 187; T., 1920, **117**, 1093, 1241. By analogy with the reactions of ferrous chloride (T., 1920, **117**, 1093), it was thought that under appropriate conditions cuprous chloride could be oxidised by sulphur dioxide in the presence of hydrochloric acid.

Experimental.

The known instability of cuprous chloride in the presence of air made it essential that special precautions should be taken to ensure that the initial solution of cuprous chloride in the hydrochloric acid should be free from any cupric salt. The following method gave excellent cuprous chloride.

Preparation of Cuprous Chloride.

Into a strong aqueous solution of cupric chloride maintained at about 90° in a water-bath a continuous stream of sulphur dioxide was passed. Cuprous chloride separated in small crystals and after several hours a good yield of the salt was obtained. The flask was then sealed and kept over-night. It was found that, unless this was done, the fine condition of the salt first produced led, on filtration, to the formatiou of a pasty mass difficult to free from cupric chloride. On keeping, however, it became much more granular, and was easily filtered and washed. The filtration was carried out with a large Gooch funnel as the containing vessel. Cuprous chloride, especially in the moist condition, is very susceptible to the action of light (Vogel). The funnel therefore was enveloped in black paper to prevent this decomposition. After a thorough washing with sulphurous acid, the white product was finally washed in a current of carbon dioxide with glacial acetic acid, alcohol, and ether respectively. It was dried as completely as possible in the current of carbon dioxide and finally in a hot air-oven, the mass being turned over at intervals. Lastly, the salt was

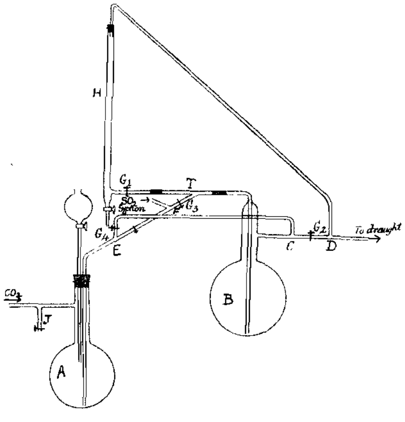
placed in a dry bottle covered with black paper, sealed, and kept in a dark place.

Apparatus.

Fig. 1 represents the apparatus used in the first experiments.

In carrying out an experiment, the whole apparatus was first filled with carbon dioxide.* To ensure the burette being properly filled with the gas, G_2 was closed with G_1 open. When this was accomplished, G_2 was opened and G_1 closed. The apparatus

FIG. 1.



having been freed from air, the current of carbon dioxide was continued and a certain quantity of the prepared cuprous chloride was introduced from a weighing bottle into the flask A. A certain volume of acid was then poured into the thistle-funnel of the flask A and the current of carbon dioxide diverted by means of the T-piece J while the acid was running on to the cuprous chloride. On gently shaking, the bulk of the cuprous chloride dissolved. The carbon

* The carbon dioxide was drawn from a cylinder. The dissolved air escapes with the first portions of the liquid volatilising; the gas subsequently emitted contains only a minimal quantity of oxygen (compare Farmer, T., 1920, **117**, 1446).

dioxide was then allowed to pass into the flask A, where it exerted a pressure and forced the solution direct into the reaction flask B. The same procedure was adopted until the whole of the cuprous chloride was dissolved in a definite volume of acid. Experiments showed that the oxidation of the cuprous salt was not measurable.

With the carbon dioxide now running through the solution, sulphur dioxide was admitted. The current of carbon dioxide was now discontinued, and the sulphur dioxide and cuprous salt were allowed to react for a definite period. In all experiments the temperature was kept constant by immersing the reaction flask in an oil-bath at 95°. At the end of the reaction the sulphur dioxide was driven out by the passage of carbon dioxide through the warm solution, and the solution cooled in a current of the gas.

Method of Analysis.

By closing clip G_3 and opening clip G_4, the carbon dioxide was diverted from the solution. On closing clip G_2 and opening G_1, the solution was driven from the reaction flask into the burette H. By closing G_1 and reopening G_2, the solution was protected from atmospheric oxidation.

To determine the degree of oxidation of the mixture, use was made of the method detailed by Rhead (T., 1906, **89**, 1491) and explained by Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," p. 55).

Ten c.c. of the cooled solution were run out of the burette H into a flask containing 10 c.c. of standard ferric alum solution, which had been acidified with concentrated hydrochloric acid and contained excess of potassium thiocyanate, and through which a current of carbon dioxide was passing. After the addition of the copper solution the contents of the flask were titrated with titanous chloride solution until the red colour of the ferric thiocyanate was just discharged. Knowing the titre of the 10 c.c. of ferric alum solution used, one could readily calculate the amount of cupric copper present in the mixture.

To determine the total copper in the solution, 5 c.c. were run directly from the burette H into a flask, water and sodium peroxide were added, and the solution was heated to boiling until chlorine was no longer evolved. The volume was then made up to 500 c.c., and 25 c.c. were used for the titration, as previously explained.

In connexion with the reaction between titanous chloride and ferric salts, Thornton and Chapman (*J. Amer. Chem. Soc.*, **1921**, **43**, 91) have specified definite conditions. The present authors'

experience substantially confirmed the main conclusions drawn by these investigators.

Description of the Phenomenon.

The solution obtained by dissolving the cuprous chloride in pure concentrated hydrochloric acid was colourless. On passing sulphur dioxide into this solution, the colour darkened immediately and became reddish-brown. On further passage of the gas, the colour continued to darken and a distinct opalescence was visible in the flask after about ten minutes. The opalescence became more pronounced as the reaction proceeded.

Quantitative Aspect of the Reaction.

When sulphur dioxide oxidises cuprous chloride in the presence of concentrated hydrochloric acid, two possible reactions may be involved. They correspond (*a*) with direct reduction of the sulphur dioxide to sulphur, (*b*) with initial reduction of the sulphur dioxide to hydrogen sulphide, which, with excess of sulphur dioxide, reacts to form sulphur. Both reactions are represented finally by the equation:

$$(1)\ 2Cu_2Cl_2 + 4HCl + SO_2 = 4CuCl_2 + 2H_2O + S$$

so that it is impossible to differentiate quantitatively between them.

To determine whether the reaction proceeded in accord with the above equation, known weights of cuprous chloride were dissolved in 250 c.c. of concentrated (33 per cent.) hydrochloric acid, and sulphur dioxide was passed into the solution for about four hours, whereby sulphur was liberated. The percentage of cupric salt was determined as described, and the sulphur estimated after the solution had been filtered through a Gooch crucible.

TABLE I.

Experiment.	Grams of copper in 250 c.c. of the cuprous chloride solution.	$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100.$	Sulphur. Found. Gram.	Sulphur. Calc. Gram.
1	5·02	3·6	0·0248	0·0252
2	7·92	5·0	0·0508	0·0498
3	8·00	5·6	0·0532	0·0563

From these results it can be concluded that the equation formulated above represents the reaction.

Influence of Concentration of Cuprous Chloride.

Varying quantities of cuprous chloride were dissolved in 250 c.c. of concentrated hydrochloric acid. Sulphur dioxide was passed through the solution for four hours, and the amount of cupric chloride subsequently estimated.

TABLE II.

Experiment	4	5	6	7	8	9
Grams of cuprous copper in 250 c.c. of acid	3·44	5·02	6·94	8·00	8·25	13·35
$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100$	2·7	3·6	4·08	5·6	6·1	7·5

These results clearly indicate that the degree of oxidation is dependent on the initial concentration of cuprous salt.

Influence of Concentration of Acid.

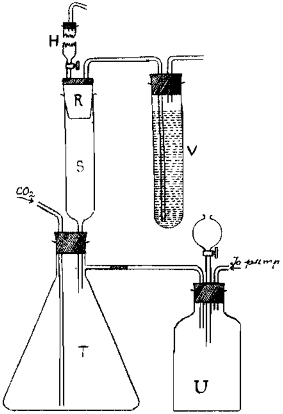
Cuprous chloride (11 grams), dissolved in 250 c.c. of acid (1 part of 33 per cent. hydrochloric acid : 1 part of water) and treated with sulphur dioxide for four hours, was oxidised to the extent of 1·8 per cent. It was noticed that in addition to sulphur, a certain amount of a black precipitate was also produced. At a lower concentration of acid (1 part of acid : 2 parts of water) the cuprous chloride no longer reacted with the sulphur dioxide so as to give a deposition of sulphur, but instead, at the end of four hours, a heavy black precipitate was formed. A qualitative examination of the precipitate indicated cuprous sulphide.

The formation of this precipitate made it a matter of great difficulty to withdraw the solution directly from the burette for analysis, and the following filtration device was therefore added (Fig. 2).

The flask, *T*, containing 10 c.c. of ferric alum, an excess of concentrated hydrochloric acid, and potassium thiocyanate, having been filled with carbon dioxide, the current of gas was discontinued and the pump slowly started. Five or ten c.c. of the solution were allowed to flow from the burette, *H*, and filtered by means of the Gooch crucible, *R*. When all the solution had filtered through, the suction drew from the tube, *V*, dilute hydrochloric acid, which thoroughly washed the precipitate free from adhering copper salt. A rapid current of carbon dioxide was now passed and simultaneously the funnel in the bottle, *U*, cautiously opened. In this way

the cuprous salt was guarded from oxidation while the pressure was being readjusted. The solution in the flask, *T*, was then titrated with the standard titanous chloride.

FIG. 2.



The results obtained are given in the following table.

TABLE III.

Duration of experiment ...... Four hours.
Solution .... Eleven grams of cuprous chloride in the acid specified in columns 2 and 3.

Experiment.	Concentrated hydrochloric acid. C.c.	Water. C.c.	Remarks.
10	250	0	Sulphur only.
11	175	75	,, ,,
12	150	100	Much sulphur + small black precipitate.
13	125	125	Sulphur + black precipitate.
14	82	168	Black precipitate only.
15	62	188	Black precipitate.
16	50	200	Small black precipitate.
17	40	210	Slight brown precipitate.
18	38	212	Slight oxidation.
19	35	215	No oxidation.
20	30	220	,, ,,

Apparently cuprous chloride in the presence of acid of smaller concentration than that used in experiment 18 is not acted on by sulphur dioxide. It also appears that there is some definite concentration of hydrochloric acid, above which cuprous chloride and sulphur dioxide react with the separation of sulphur only, an intermediate concentration of acid in which both sulphur and the black sulphide are precipitated, and a final stage in which the sulphur dioxide reacts to give the sulphide only.

In experiments 14 and 15, analysis showed that when the precipitate was washed with dilute hydrochloric acid and then with air-free water and dried, it still contained large and variable quantities of chloride. When, however, a concentrated solution of sodium chloride was used instead of the hydrochloric acid, the amount of chloride in the precipitate was negligible, and analysis gave percentages of copper and sulphur in close accord with those required by the formula Cu_2S (Found Cu = 78·7; S = 21·3. Calc., Cu = 79·8; S = 20·1 per cent.).

Degree of Oxidation in a Special Case.

With the apparatus shown in Fig. 2, the following results were obtained.

TABLE IV.

Duration of experiment	Four hours.		
Solution	Eleven grams of cuprous chloride in 250 c.c. of acid (82 c.c. of concentrated hydrochloric acid and 168 c.c. of water).		
Experiment	21	22	23
$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100$	1·5	1·24	1·30

The above are results of experiments in which the black cuprous sulphide was deposited. It might be expected that in view of the withdrawal of one of the products of the reaction the degree of oxidation would have been greater. This, however, is not supported by the experimental evidence.

Limit of Reduction of Cupric Chloride by Sulphur Dioxide in Concentrated Hydrochloric Acid Solution.

It has been shown by Wardlaw and Clews (T., 1920, **117**, 1099) that ferric chloride dissolved in excess of hydrochloric acid is incompletely reduced by sulphur dioxide. It was thought that cupric chloride might behave similarly. Solutions were prepared

with a constant copper content but having as constituents varying percentages of cupric and cuprous chlorides.

TABLE V.

Concentration .... 0·33 Gram of copper in 250 c.c. of concentrated (33 per cent.) hydrochloric acid.
Duration of experiments ...... Four hours.

Experiment.	$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100.$ Initial value.	Final value.	Remarks.
24	100	22·2	Sulphate formed.
25	22	16·5	,, ,,
26	15	7·5	,, ,,
27	9·8	8·8	,, ,,
28	6·79	7·14	No sulphate.

TABLE VI.

Duration of experiments ... Four hours.

Experiment.	Grams of total copper in 250 c.c. of acid.	$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100.$ Initial value.	Final value.	Remarks.
29	3·516	100	56·69	Sulphate formed.
30	3·903	57	38·0	,, ,,
31	5·477	28·7	26·39	,, ,,
32	4·541	28·06	20·35	,, ,,

Results (31) and (32) show that whilst at the concentration of copper employed in experiment 31, equilibrium is nearly attained, *in experiment 32 such is not the case. From the above tables it* can be readily seen that in concentrated hydrochloric acid sulphur dioxide does not effect a complete reduction. Instead, there is established, depending on the concentration of total copper, an equilibrium between the cuprous and cupric salts present.

Reaction of Sulphur with Cuprous Chloride.

In a paper by Vortman and Padberg (*Ber.*, 1889, **22**, 2642), in which are references to earlier work on the subject, it is shown that if an acid solution of cuprous chloride is boiled with flowers of sulphur, the reaction may be interpreted by the equation :

$$Cu_2Cl_2 + S = CuS + CuCl_2.$$

The present anthors find that when finely divided sulphur is heated with cuprous chloride in dilute hydrochloric acid (112 c.c. of 33 per cent. acid and 138 c.c. of water) at 95° in a current of carbon dioxide, a black precipitate is slowly formed. From qualitative evidence, this precipitate undoubtedly contains a large proportion of cuprous

sulphide. However, attempts to obtain a sufficient quantity for analysis have so far proved futile, as the sulphide forms a coating on the free sulphur and brings the reaction to a standstill. The yield after seventy-two hours was very minute. In the paper by Vortman and Padberg no mention is made of the use of an inert atmosphere, the temperature of their experiments was much higher than ours, and, lastly, the sulphide was not specially isolated and analysed.

Some results by Rammelsberg and Huntington (*Eng. and Min. J.*, 1882, **34**, 150) in connexion with the Patio process seem germane to this subject. They showed that if silver sulphide and cupric chloride are made to act on each other in the presence of air and sodium chloride solution, either cuprous chloride, silver chloride, and sulphur are produced, or the cuprous chloride formed becomes converted into a sulphide:

$$Ag_2S + 2CuCl_2 = 2AgCl + Cu_2Cl_2 + S.$$
$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S.$$

The liberation of sulphur, however, is a secondary reaction taking place only to a very limited extent:

$$Ag_2S + CuCl_2 = 2AgCl + CuS.$$
$$CuS + CuCl_2 = Cu_2Cl_2 + S.$$

The amount of cuprous chloride formed and of sulphur set free is dependent on the strength of the solvent, the temperature, and the presence of air.

The last equation is distinctly interesting, as it represents the reverse of the reaction investigated by Vortman and Padberg (*loc. cit.*). Incidentally, the presence of air plays an important part.

Reaction of Sulphur with Cupric Chloride.

Fihlol and Senderens (*Compt. rend.*, 1881, **93**, 152) state that when the sulphate, nitrate, and chloride of copper respectively are heated with sulphur, no sensible decomposition occurs. This statement substantially confirms the results of experiments carried out by the authors in which cupric chloride in the presence of water and of dilute hydrochloric acid (112 c.c. of 33 per cent. acid : 138 c.c. of water) respectively was heated with sulphur for fonr hours in a current of carbon dioxide. It was found that no reaction had taken place. In the presence of concentrated hydrochloric acid, however, under the above conditions, a reduction of about 5 per cent. was effected and sulphuric acid was detected in the solution. The following equation therefore represents the reaction:

$$6CuCl_2 + S + 4H_2O = 3Cu_2Cl_2 + 6HCl + H_2SO_4.$$

Discussion of Results.

The oxidation of cuprous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid has been shown to be represented by the equation :

$$(1) \quad 2Cu_2Cl_2 + SO_2 + 4HCl = 4CuCl_2 + 2H_2O + S.$$

Moreover, experiments have also shown that cupric chloride in the presence of concentrated hydrochloric acid is reduced by sulphur with the production of sulphuric acid. This may be represented by the equation :

$$(2) \quad 6CuCl_2 + S + 4H_2O = 3Cu_2Cl_2 + 6HCl + H_2SO_4.$$

From these facts it seems justifiable to assume that the first equation is reversible. This reversibility is normally obscured by the reaction represented in equation (2).

No sulphuric acid was ever detected when sulphur dioxide oxidised cuprous chloride in the presence of hydrochloric acid. We may therefore say that in reactions in which sulphur alone is precipitated, the reversible equation (1) represents the course of the reaction. This idea of a reversible reaction receives support from the fact that complete reduction of cupric solutions does not occur when sulphur dioxide reacts in the presence of concentrated hydrochloric acid. Instead, there seems to be established equilibrium solutions of cupric chloride–cuprous chloride in which sulphur dioxide does not produce any effect.

With reference to those reactions in which the black sulphide was precipitated, two possible explanations suggest themselves. This deposition may be due to a secondary reaction between the cuprous chloride and hydrogen sulphide produced by the reduction of the sulphur dioxide or between the cuprous chloride and sulphur initially formed. The authors are of opinion that there seem to be no special grounds for supposing that the sulphur dioxide undergoes direct reduction to hydrogen sulphide in these reactions, and consider that the precipitation is due to a secondary reaction between the cuprous chloride and the sulphur initially produced, as shown by the authors' experiments :

$$(3) \quad S + 2Cu_2Cl_2 = 2CuCl_2 + Cu_2S.$$

Owing to the continual disturbance of the eqnilibrium by the reaction represented in equation (3) one might expect a comparatively high degree of oxidation from this reaction. Reference to Table IV, however, shows that this is not so. This result can, however, be accounted for by a consideration of the oxidation

potentials of cuprous–cupric mixtures and of sulphurous acid. Each of these cuprous–cupric chloride mixtures has a definite oxidation potential, and it is the establishment of an oxidation potential equal to that of the sulphurous acid in the special acid concentrations that brings about the equilibrium value. It follows, therefore, that the ratio of cupric to cuprous chloride in a solution is the sole factor determining the amount of oxidation. As regards equation (1), therefore, once this definite ratio of cupric to cuprous salt is obtained, no further oxidation will take place, and as no further liberation of sulphur will occur, reaction (3) will cease to be operative.

To explain the increase in percentage oxidation with increase in the concentration of cuprous chloride recorded in Table II, a reference to some work by Poma (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 192) seems to furnish the necessary data. He found that for a definite concentration of hydrochloric acid, as the concentration of cupric chloride increased, the amount of cuprous chloride which could be dissolved increased enormously, whilst the number of free cuprous ions showed only a very small increase, indicating that the cuprous copper was present in the form of a complex ion. From these results it may be stated that if we are to establish a mixed cuprous–cupric solution the potential of which will be equal to that of the sulphur dioxide in a given concentration of acid, a greater amount of cupric salt must be produced in the more concentrated than in the more dilute cuprous chloride solutions before the necessary free cupric ions will be present to give the requisite oxidation potential.

Summary.

1. The oxidation of cuprous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid can be represented, as regards its quantitative aspect, by the equation:

$$2Cu_2Cl_2 + SO_2 + 4HCl = 4CuCl_2 + 2H_2O + S.$$

2. The degree of oxidation is dependent on the initial concentration of cuprous chloride.

3. Oxidation by sulphur dioxide does not occur in solutions of cuprous chloride containing less than 38 c.c. of free hydrochloric acid (33 per cent.) in 250 c.c. of solution, and immersed in an oil-bath at 95°.

4. Oxidation by sulphur dioxide in solutions of cuprous chloride containing more than 150 c.c. of hydrochloric acid (33 per cent.) in 250 c.c. of solution results in precipitation of sulphur. In solutions containing between 150 c.c. and 112 c.c. of concentrated acid in

250 c.c. of solution the precipitate consists of sulphur and cuprous sulphide, whilst in solutions containing between 112 c.c. and 38 c.c. of concentrated acid in 250 c.c. of solution the precipitate is cuprous sulphide alone.

5. With decreased concentration of acid the degree of oxidation is lowered, and even in experiments where the black cuprous sulphide is precipitated the degree of oxidation is still very small.

6. In the presence of concentrated hydrochloric acid sulphur reduces cupric chloride with the production of cuprous chloride and sulphuric acid. In dilute acid and aqueous solutions, this reduction does not occur.

7. There is distinct evidence that when cuprous chloride reacts with sulphur in the presence of dilute hydrochloric acid at approximately 95° in a current of carbon dioxide, cuprous sulphide is produced.

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XXVII.—*The Ultimate Composition of British Coals.*

By THOMAS JAMES DRAKELEY.

THE ultimate analyses of British coals which are available are somewhat limited in number, and therefore this paper is of a tentative nature, and may require revision as more data are accumulated. However, with the figures in hand there appears to exist a more or less definite relationship between the composition of coal and its properties, and in all probability with further research the relationship will be more accurately ascertained.

As a rule, the ultimate analysis of an air-dried coal is expressed in terms of the percentage of carbon, hydrogen, nitrogen, sulphur, ash, moisture, and oxygen. The percentage of oxygen is obtained as the difference between 100 and the sum of the percentages of the other constituents.

Up to the present, the occurrence of nitrogen in coal has been found to conform with no known laws. In bituminous coals, the quantity is unusually constant, and averages about 1·3 per cent.,

whereas in anthracite probably about 0·6 per cent. may be accepted as an average figure.

The mineral matter and sulphur are both more or less fortuitous constituents of coal, and the proportions in which they are present vary over wide ranges.

There is a certain percentage of moisture which cannot be removed from coal by air-drying. This fraction needs more drastic treatment for its removal, and there appears to exist a relation between the type of coal and the quantity of inherent water (Porter and Ralston, Technical Paper 113, 1915, Bureau of Mines, U.S.A.).

The methods of estimating the water in coal are numerous, and no one method seems to have been adopted as a standard in this country. Consequently, the available values for the moisture contents of British coals appear to be useless, as in most cases no indication is given of the method of estimation.

The three fundamental elements composing coal are carbon, hydrogen, and oxygen; and for the purposes of this paper the ultimate composition of the various coals has been expressed in terms of these three elemental components.

As the constitution of a coal is determined by three partly dependent variables only, it is possible to represent the composition of a given sample by a point on the triangular co-ordinate principle. This method was first applied to coal analyses by Grout (*Econ. Geol.*, 1907, **2**, *225*), and was further developed by Ralston (Technical Paper 93, 1915, Bureau of Mines, U.S.A.).

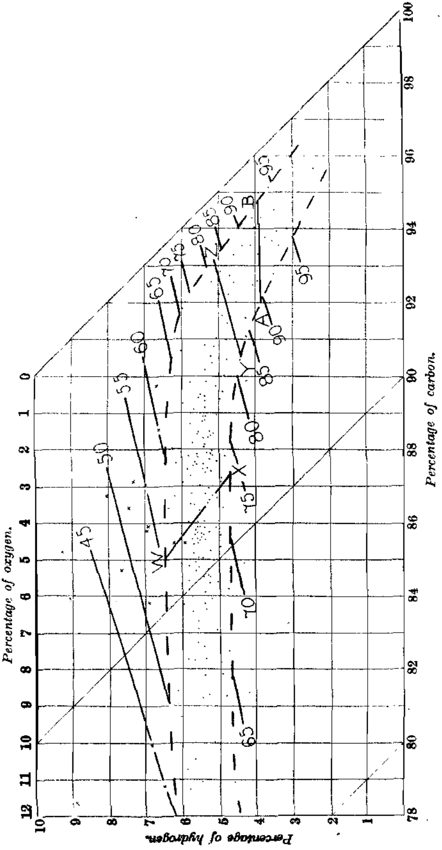
In this investigation, the compositions of coals in terms of carbon, hydrogen, and oxygen were represented by points in a right-angled isosceles triangle *LMN* (right angle at *L*, vertical *LM*, hypotenuse *MN*, base *NL*, clockwise).

Since the percentage of oxygen was obtained by difference, the probable errors in its value were greatest, and it was therefore represented on the smallest scale, that is, as a distance from the hypotenuse *MN*. The percentage of carbon and of hydrogen was represented as a distance from the vertical side *LM*, and from the base *NL* respectively.

When the points representing the ultimate analyses of the coals were plotted in the above manner, it was found that all the points lay in a remarkably narrow band within the angle *MNL*. This portion of the figure has been enlarged and forms Fig. 1.

Of the 287 points entered on the figure, 230 represent analyses of British coals which have been published ("The Analyses of British Coals and Cokes," compiled by Greenwell and Elsden; "The Calorific Power of Fuels," by Poole; "Coal and its Scientific Uses,"

FIG. 1.


Percentage of oxygen.
Percentage of carbon.
Percentage of hydrogen.
W
X
Y
Z
A
B

by Bone; *Journals of the Chemical Society* and the *Society of Chemical Industry*).

Classification.

Despite the fact that no standard methods of coal analysis have been adopted in the British Isles, the results exhibit fair regularity, and it is possible to group the coals in classes. Thus, within the area of the band enclosed by the lines *WX* and *YZ*, occur the coking coals. The coals of anthracitic nature occupy the area to the right of the line *YZ*, whereas the non-coking coals of low carbon content are on the left of *WX*, and are separated from the lignites by a line (not shown on Fig. 1) which is apparently almost parallel to the oxygen-content co-ordinates, and meets the carbon axis at the point representing 78 per cent.

The anthracitic coals are capable of being divided into two distinct classes by the line *AB*. The coals to the right of *AB* are true anthracites, whilst those in the area *ABZY* are more usually termed steam coals.

It may be observed that the line *AB* almost represents the ratio of carbon to hydrogen which equals 24, and is the only line of demarcation which approximates to a fixed carbon : hydrogen ratio. Hence it would appear to be impossible to classify coals satisfactorily by means of the carbon : hydrogen ratio.

The position of the true anthracites at the end of the band beyond the line *AB* would seem to be evidence against Strahan and Pollard's conclusion (*Mem. Geol. Survey England and Wales*, 1915, **6**, 91) that anthracites differ from other coals, such as steam coals, in the original nature of their plant accumulations. If such original differences existed, it would not appear likely that anthracites would fall normally at the end of the band in a position immediately contiguous to the steam coals. By analogy with the cannel coals, a more anomalous position would be anticipated.

If the diagram be extended to include lignite, peat, and wood, it will be found that the band is continuous, and that each type of fuel falls into a definite position generally within the band. The continuity of the band appears to uphold the theory that the coal-age plants were of exactly similar chemical nature to the vegetation of the present time.

As each type of coal occupies a definite area of the diagram, it would seem to be a satisfactory method of classification. In this connexion it may be noted that none of the other suggested systems of classifying coals is satisfactory (compare Stopes and Wheeler, "The Constitution of Coal," p. 42; Bone, "Coal and its Scientific Uses," p. 63). No doubt this is due to the fact that the dividing

lines between the groups have no obvious relation to such factors as the percentage of carbon, hydrogen, fixed carbon, etc.; and therefore no completely satisfactory mathematical means is likely to be devised for calculating, from any of the values of an analysis, a number which shall indicate with certainty the properties of the coal.

It may be objected that such a graphical classification is not in accord with the statement that two quite dissimilar coals may have almost identical chemical compositions. However, isomeric compounds are so common among very simple organic compounds that it is quite likely that isomerides exist among such complex compounds as are included under the heading of coal. The author cannot quote any examples of such isomerism, and is led to infer that coals of different types with the same chemical composition will be of rare occurrence. In this connexion, reference may be made to a paper by Bone and Sarjant (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 128) in whioh mention is made of two coals having different properties, but nearly the same percentage composition. Their ultimate compositions are given in columns two and three of Table I, whilst in columns four and five, the compositions are expressed in terms of carbon, hydrogen, and oxygen.

TABLE I.

	Durham coking coal.	Barnsley hard steam coal.	Durham coking coal.	Barnsley hard steam coal.
Carbon	83·73%	82·33%	87·12%	86·63%
Hydrogen	4·76 ,,	4·99 ,,	4·95 ,,	5·25 ,,
Nitrogen	1·09 ,,	1·50 ,,	—	—
Sulphur	1·28 ,,	0·70 ,,	—	—
Ash	1·62 ,,	2·76 ,,	—	—
Oxygen	7·52 ,,	7·72 ,,	7·93 ,,	8·12 ,,
	100·00	100·00	100·00	100·00

When the points representing the compositions of these two coals were placed on the figure, it was found that they were close to the boundary line *WX*, but were distinct. This suggests that the exact position of this line separating coking from non-coking coals will finally be determined by analyses of almost similarly constituted coals having different properties. Furthermore, the case upholds Ralston's statement (*loc. cit.*, p. 17) that the lines of demarcation between the classes of coals will be fairly sharply defined.

Cannel Coal.—The only exception to the generalisation that the various classes of coals occupy definite regions within the band was afforded by the cannel coals. The points representing their compositions are indicated on the diagram by crosses, and it is seen that

they are situated in a disperse region mainly above and possibly within the band. The anomalous position of the cannel coals shows that they are a race apart from the other coals. Their original parent-substance appears to have been essentially different from that producing the ordinary type of coals; and as the area occupied on the diagram by the cannel coals corresponds roughly with that in which the fossil resins would occur, it seems that the parent-substance was more or less composed of highly resinous spores (compare Arber, "The Natural History of Coal").

Fixed Carbon Content.

Although it has been shown (Bone and Silver, T., 1921, **119**, 1145) that the customary methods of estimation of the volatile matter, and hence the fixed carbon, are liable to give slightly erroneous results, the available figures are such that lines may be drawn with fair accuracy through positions representing coals which yield the same percentage of fixed carbon on carbonisation. The lines are straight, and pass diagonally across the diagram. To avoid confusion, the position of each line is indicated by straight lines drawn outside the coal band; and the figures placed at the end of each line give the percentage of fixed carbon yielded by the coals lying along that line.

It was not found possible to draw similar lines joining the points representing the coals of the same calorific value, owing to insufficient trustworthy data being available. The calorific values in hand were irregular, probably owing to the method of estimation (Drakeley, *Trans. Inst. Min. Eng.*, 1918—1919, **56**, ii, 51). Unless a calorimeter of the bomb type is used, the numerical value is not sufficiently accurate for the purposes of determining the positions of the lines on the coal band. From the author's experiments it would appear that the corresponding lines for equal calorific value will slope in the opposite direction to the fixed carbon content lines (compare Ralston, *loc. cit.*). The determination of the position of the lines of equal calorific value is a matter of importance, since if the calorific value and the percentage of fixed carbon are known, the intersection of the two representative lines on the diagram will give with fair accuracy the ultimate composition of the coal.

Variations in Coal Seams.

An investigation was commenced to determine whether increased age would cause the representative point to be moved along the band towards the anthracite end. Samples of coal from near the roof,

middle, and bottom of a Lancashire seam were collected from a vertical section, and analysed. The results are given in Table II, together with additional figures for a Yorkshire coal.

TABLE II.

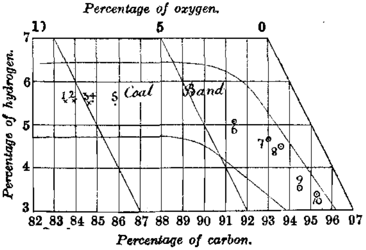
Compositions of Samples of Coal from Different Parts of the Same Seam.

	Lancashire seam.			Yorkshire seam.*	
Position in seam:	Top.	Middle.	Bottom.	Top.	Bottom.
C per cent.	79·12	79·71	81·81	73·36	71·62
H	5·24	5·28	5·32	4·80	4·57
N	1·33	1·33	1·34	1·34	1·24
S	0·86	0·87	0·65	1·37	2·81
Ash.	3·15	2·81	1·39	5·60	6·64
Water.	0·00	0·00	0·00	5·17	5·91
O	10·30	10·00	9·49	8·36	7·21
Total.	100·00	100·00	100·00	100·00	100·00
Fixed carbon per cent.	59·52	60·29	63·21	—	—
C per cent.	83·58	83·91	84·67	84·79	85·87
H	5·54	5·56	5·51	5·55	5·48
O	10·88	10·53	9·82	9·66	8·65
Total.	100·00	100·00	100·00	100·00	100·00
Reference No.	1	2	3	4	5

* Analysts: J. and H. S. Pattinson.

The results, when plotted, appear to indicate that the influence of age, and such other geological influences as are involved, cause

FIG. 2.



the point to be slightly displaced towards the anthracite end, in a direction roughly parallel to the coal band. The numbers on Fig. 2 correspond with the reference numbers given in Tables II and III.

Illingworth (*Proc. Sth. Wales Inst. Eng.*, 1921, **36**, 355) has analysed a series of samples of coal obtained from the Nine-foot Seam in South Wales, at various points travelling from east to west along the seam. The seam, no doubt, is of the same geological age throughout, but the ultimate compositions show a fairly regular transition towards anthracite.

From the results of Illingworth's analyses, the composition of the various samples, in terms of carbon, hydrogen, and oxygen, have been calculated, and are given in Table III.

TABLE III.

Composition of Samples of Coal from the Nine-foot Seam, South Wales (Illingworth).

C per cent.	91·42	93·03	93·61	94·53	95·32
H	5·12	4·65	4·47	3·51	3·38
O	3·46	2·32	1·92	1·96	1·30
Total.	100·00	100·00	100·00	100·00	100·00
Reference No.	6	7	8	9	10

The position of the points (Fig. 2) seems to indicate that the cause which has produced, in the former cases, the displacement of the composition in a direction parallel to the band has also been acting in a somewhat similar manner throughout the length of the seam in South Wales. Hence it would appear that the geological conditions, possibly pressure, may be the principal agent in the production of the change in the ultimate composition of the coal; and that age may not be so important a factor.

Owing to the prolonged coal strike during last session, further work was impossible. The investigation is now proceeding, and further comment is reserved for a later communication.

The Effect of Heating a Non-caking Bituminous Coal in a Vacuum.

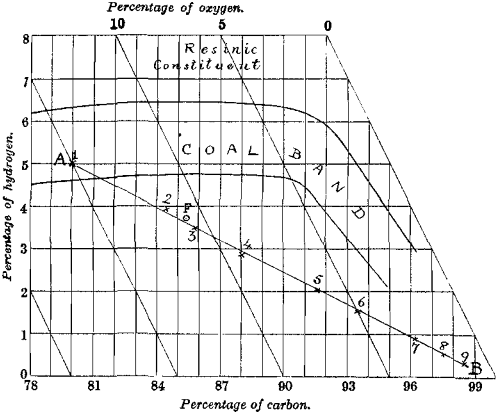
Former papers on the effect of heating samples of coal under various conditions have been largely concerned with the volatile gaseous and liquid constituents, as distinct from the solid carbonised residual coke. In this paper, the ultimate compositions of the residual cokes obtained from a sample of a Leicestershire non-caking coal by heating in a vacuum to various temperatures receive main attention, and are represented in the graphical manner already described.

A large sample of a Leicestershire non-caking coal was powdered to pass through a sieve of mesh 30 to the inch, and was thoroughly mixed. From this bulk, small charges of about 8 grams were

introduced into a long silica test-tube which was connected with a scrubber-tower filled with asbestos fibre to prevent the liquid volatile constituents from passing into the filter-pump operated with high-pressure water. The pressure within the silica tube was measured by means of a manometer, and ranged from 15 to 20 mm. during the experiments.

The silica tube was introduced into a tubular electric furnace, and the temperature was very slowly raised to avoid an explosive evolution of the volatile matter from the coal. When the required

Fig. 3.



Graphical representation of the decomposition of a non-caking coal on heating.

temperature was attained, it was kept constant for nine hours to ensure the whole of the charge of coal being heated throughout.

The sample of coke was allowed to cool in the vacuum, weighed, and then analysed completely. In Table IV are given the ultimate compositions of the original coal and of the samples of coke obtained from the coal by heating in a vacuum to the specified temperatures. The percentage yields of coke at the various temperatures are given, and also the percentage composition expressed in terms of carbon, hydrogen, and oxygen.

The final set of figures was then plotted in the way described above,

TABLE IV.—*Ultimate Compositions of Original Coal and Cokes.*

	Original coal.	Residual coke. Temperature. 370°.	420°.	510°.	650°.	750°.	900°.	1000°.	1200°.
C per cent.	76·72	80·97	82·12	84·14	87·35	89·09	91·53	92·76	93·77
H	4·80	3·76	3·34	2·75	1·97	1·48	0·78	0·50	0·22
N	1·58	1·42	1·39	1·35	1·32	1·32	1·30	1·29	1·25
S	0·89	0·77	0·76	0·76	0·79	0·80	0·82	0·82	0·81
Ash	1·63	2·01	2·17	2·31	2·50	2·63	2·73	2·75	2·78
O	14·38	11·07	10·22	8·69	6·07	4·68	2·84	1·88	1·17
Total.	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Yield of coke on carbonising.	100·00	81·22	75·22	70·43	65·15	62·07	60·21	59·20	58·53
C	80·00	84·52	85·83	88·03	91·57	93·53	96·20	97·50	98·54
H	5·01	3·93	3·49	2·88	2·07	1·56	0·82	0·53	0·23
O	14·99	11·55	10·68	9·09	6·36	4·91	2·98	1·97	1·23
Total.	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Reference No.	1	2	3	4	5	6	7	8	9

TABLE V.—*Residual Carbon, Hydrogen, Oxygen, Nitrogen, and Sulphur in the Cokes obtained from 100 grams of Coal.*

	Original coal.	Cokes. Temperature. 370°.	420°.	510°.	650°.	750°.	900°.	1000°.	1200°.
Residual C.	76·72	65·76	61·77	59·26	56·91	55·30	55·11	54·91	54·88
Percentage.	100·00	85·72	80·51	77·24	74·18	72·08	71·83	71·58	71·53
Residual H.	4·80	3·05	2·51	1·94	1·28	0·92	0·47	0·30	0·13
Percentage.	100·00	63·62	52·34	40·35	26·74	19·14	9·78	6·17	2·68
Residual O.	14·38	8·99	7·69	6·12	3·95	2·90	1·71	1·11	0·68
Percentage.	100·00	62·52	53·46	42·56	27·50	20·20	11·89	7·74	4·76
Residual S.	0·89	0·63	0·57	0·54	0·51	0·50	0·49	0·49	0·47
Percentage.	100·00	70·3	64·2	60·1	57·8	55·8	55·5	54·8	54·5
Residual N.	1·58	1·15	1·05	0·95	0·86	0·82	0·78	0·76	0·73
Percentage.	100·0	73·0	66·2	60·2	54·4	51·9	49·5	[illegible]	[illegible]

when it was observed that, within the limits of experimental error, ill the points lay on a straight line *AB* (Fig. 3). The points in this igure are numbered to correspond with the reference numbers given in Table IV.

Discussion of the Results.—According to Wheeler, coal contains wo distinct types of compounds, one of which, the resinic, decomposes more readily than the other, the cellulosic compound. The composition of the two constituents obtained by extraction with pyridine was not determined, and therefore cannot be represented by two points on Fig. 3. It is sufficient for the purpose of this paper, however, to note that a resinic constituent would contain a relatively high percentage of hydrogen, and would be represented on the diagram by a point above the line *AB* and possibly in the vicinity of the area indicated in Fig. 3 (compare Clark and Wheeler, T., 1913, **103**, 1704). The cellulosic constituent would be represented n a position below the line *AB*. If the resinic compound decomposes first, the line of decomposition would not be straight, but would tend to curve downwards towards the cellulosic constituent. Hence, since the line of decomposition is straight, it would suggest hat such preferential decomposition of the two constituents failed o occur in this case.

The ultimate compositions of the residual cokes gave no indication of a "critical temperature" between 700° and 800°, where the ignificant increase in the proportion of hydrogen in the gaseous products is generally noted; this increase is adduced as evidence of he existence in the coal conglomerate of a compound stable up to 50° (Burgess and Wheeler, T., 1910, **97**, 1917, *et seq.*).

Percentage of Carbon, Hydrogen, Oxygen, Nitrogen, and Sulphur in he Coal, and Coked Residues.—The residual carbon, hydrogen, oxygen, nitrogen, and sulphur in the residues from 100 grams of coal were obtained in each case as the product of the yield of coke and he percentage of the particular element (see Table IV). These values are given in Table V, and are further calculated as percentages. The latter have been plotted in Fig. 4.

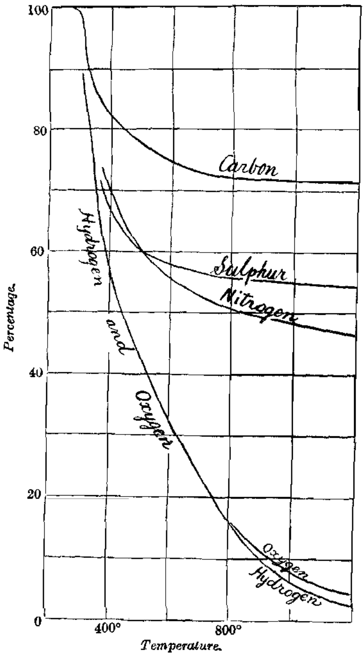
The figure shows that the volatile portions of each element are volved smoothly throughout the whole range of temperature, and hat there is no break in any of the curves between 700° and 800° to ndicate the decomposition of a new "hydrogen-yielding" constituent.

As far as could be judged, the samples of coal commenced to decompose between 275° and 300°.

Sulphur.—From the diagram (Fig. 4) it is seen that the sulphur s evolved very rapidly at the lower temperatures, but the elimination s much less rapid at higher temperatures.

The ash of the coal (1·63 per cent.) was pale grey, which indicated that iron pyrites was almost entirely absent; also, as the amount of sulphur left in the ash amounted only to 2·13 per cent. (0·03 per

FIG. 4.



Percentage evolution of elements from coal on heating.

cent. of the coal) when the coal was incinerated at a very gentle heat, it would appear that almost the whole of the sulphur was present in the form of an organic compound.

Since the sulphur was rapidly eliminated, it indicated that one of the first substances to decompose was the sulphur-bearing compound. The sulphur in plants is usually associated with the nitrogen in the proteins, and from Fig. 4 it is observed that the nitrogen was also evolved rapidly at the lower temperatures. It would therefore seem that the nitrogenous matter was one of the constituents of the coal conglomerate which decomposed first on heating.

Nitrogenous Matter.—The proteins contain a relatively higher percentage of hydrogen than cellulosic substances, and a lower percentage than the resins. Therefore, if it is accepted that the proteid matter is easily decomposed by a gentle heat, then a cellulosic constituent containing a lower percentage of hydrogen must decompose at the same time in order to give a total average decomposition of the coal substance which shall be represented hy a straight line. Since coal is considered to be a conglomerate of three types of compounds, resinic, cellulosic, and nitrogenous, it would appear that in tbis particular case the first effect of heat was to decompose the nitrogenous constituent and part of the cellulosic constituent. Illingworth (*Proc. Sth. Wales Inst. Eng.*, 1920, **36**, 23) shows that the β-cellulosic compounds are easily decomposed.

The decomposition of tbe nitrogenous derivatives apparently decreased to a relatively slow rate above 450°. The two remaining constituents, the more resistant cellulosic (α-cellulosic ?) and resinic derivatives, then decomposed conjointly in a manner similar to the above.

It would therefore seem that the cellulosic substances decomposed more or less steadily throughout the whole range of temperature.

From other experiments, the elimination of the nitrogen and sulphur from the coal substance appears to be influenced by the inorganic matter present in the coal. Experiments are now being made in this connexion, and will be dealt with in a later paper.

Hydrogen.—As the ultimate analyses of the cokes obtained from this sample of coal failed to show any evidence of a critical temperature between 700° and 800°, analyses were made of samples of gas collected between 400° and 600°, and between 800° and 900°. The results are given in Table VI, and show that hydrogen predominated in the gas collected between 800° and 900° (compare Burgess and Wheeler, *loc. cit.*).

Whilst the regular continuity of the curves shown in Figs. 3 and 4 fails to give any evidence of the selective decomposition below 750° of one constituent of the coal conglomerate to yield mainly paraffins, and above 750° of another constituent to yield mainly hydrogen, a feasihle explanation of the phenomena appears possible.

TABLE VI.

Composition of Gas.

Calculated as "nitrogen-free" gas.

Temperature range.	400° to 600°.	800° to 900°.
Carbon dioxide	4·1 per cent.	1·9 per cent.
Ethylenes.	5·1 ,,	3·5 ,,
Carbon monoxide.	8·7 ,,	16·4 ,,
Paraffins.	59·3 ,,	21·7 ,,
Hydrogen.	22·8 ,,	56·5 ,,

The actual constituents in the volatile matter at any given temperature are determined by the rate at which each element is being evolved at that temperature. If, below 750°, the carbon content of the volatile matter is relatively high, hydrocarbons would be expected to constitute a large proportion of the gaseous matter, particularly as the hydrocarbons are stable below that temperature. Similarly, if hydrogen is the chief element of the total volatile matter above 750°, then it would be anticipated that hydrogen would be the principal gas.

In order to test this suggestion, at selected temperatures, the slopes of the respective tangents to the curves shown in Fig. 4 were determined as accurately as possible. From these results, the approximate percentage elemental constitutions of the total volatile matters evolved at those temperatures were calculated. The values, which are only approximate owing to the method of estimation, are given in Table VII in atomic percentages. That is, for instance, at 700°, the rate at which the three chief elements of the volatile matter were evolved was such tbat sixteen atoms of carbon were eliminated with seventy-one atoms of hydrogen and thirteen atoms of oxygen.

TABLE VII.

Approximate Concentration (Atomic) of the Elements in the Volatile Matter.

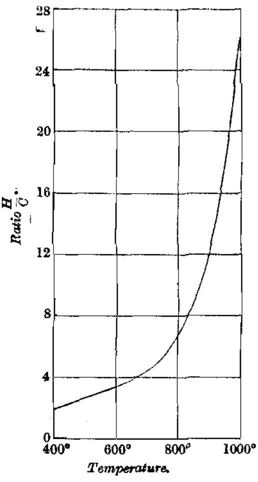
Temperature.	Carbon.	Hydrogen.	Oxygen.	Ratio $\frac{\text{Hydrogen}}{\text{Carbon}}$.
400°	31·0	58·0	11·0	1·9
500	24·5	63·5	12·0	2·6
600	20·0	67·5	12·5	3·4
700	16·0	71·0	13·0	4·4
800	10·8	75·8	13·4	7·0
900	6·4	79·4	14·2	12·4
1000	3·2	82·4	14·4	25·8
1100	1·5	84·5	14·5	56·0

From the table, it is seen that the atomic concentration of the carbon decreases, whereas the atomic concentration of the hydrogen

increases. The oxygen does not vary over a wide range. Hence, whilst at low temperatures derivatives of carbon may largely constitute the gaseous volatile products, hydrogen will be the main gaseous product at high temperatures.

To study the influence of temperature in greater detail, the ratio of the atomic rates of evolution of hydrogen to carbon was plotted against the temperature (see Fig. 5). The curve shows a marked

FIG. 5.



change of direction between 700° and 800°. This indicates that at temperatures above 750° it is to be anticipated that hydrogen will be the principal constituent of the gas. The author does not consider the change of direction to be due to the sudden decomposition of a particular hydrogen-yielding constituent, particularly as 91 per cent. of the total volatile matter had been evolved, indicating that the decomposition of the coal was almost complete, and therefore that no main constituent of the coal was likely to have remained undecomposed up to 750°. The decomposition of a new constituent

would have been evident from the curves in Figs. 3 and 4. In addition, Fig. 4 shows that, whilst the percentage evolutions of oxygen and hydrogen from the coal were identical up to about 750°, above that temperature the oxygen rate was a little lower than the hydrogen rate. Hence the percentage of free hydrogen in the volatile products would be slightly increased on the latter account.

Fusain.

On the bedding planes of a sample of coal used in this investigation was found a quantity of friable fibrous fusain, which was carefully removed and analysed (see Table VIII).

It is peculiar that, when the composition of the fusain expressed in terms of carbon, hydrogen, and oxygen, is represented on the triangular co-ordinate diagram, the point F (see Fig. 3) should fall almost on the line *AB* of decomposition of this particular coal.

TABLE VIII.

The Ultimate Composition of Fusain.

Carbon, per cent.	78·36	85·41
Hydrogen	3·41	3·72
Nitrogen	1·10	—
Sulphur	0·83	—
Ash	6·33	—
Oxygen	9·97	10·87
	100·00	100·00

Indeed it would appear that a similarly constituted substance might be produced by heating the coal in a vacuum at 400°. However, according to Stopes and Wheeler ("The Constitution of Coal," 1918, p. 22), it is unlikely that fusain has been produced from coal by the action of heat, and consequently its position outside the normal coal band would appear to indicate that the original plant debris from which it had been formed differed from that yielding the normal coal (compare Stopes, *Proc. Roy. Soc.*, 1919, [*B*], **90**, 470). Cannel coal and fusain therefore seem to result from two totally distinct types of plant remains. In the former case, the product contains a relatively high proportion of hydrogen, whereas in the latter the percentage of hydrogen is comparatively low.

An investigation is now being made of the effect of heating other types of coal in a vacuum and also under increased pressure.

The Radium Content.

[With FREDERICK WILLIAM SMITH].

Experiments have been made with a view to determine whether any relationship exists between the radium content of a coal and its ultimate composition.

Fletcher (*Phil. Mag.*, 1912, [vi], **23**, 279) has shown that with the exception of calcareous rocks all types of sedimentary rocks have approximately the same radium content. An examination of various coals, however, has indicated that the quantity of radium bears no relationship to the percentage of any other element composing the coal substance, and furthermore varies considerably from coal to coal, even of the same class (compare Lloyd and Cunningham, *Amer. Chem. J.*, 1913, **50**, 47; Moureu and Lepape, *Compt. rend.*, 1914, **158**, 598).

About 40 grams of each sample of coal were powdered, and burnt to an ash in a muffle furnace. The temperature of the furnace was kept as low as possible, since the ash produced at a moderately low temperature was found to be more readily soluble than that resulting from heating to a high temperature.

To obtain a solution of the incinerated mineral matter it was repeatedly extracted with small quantities of hydrochloric acid, but in two cases a trace of a white residue, presumably silica, remained, which was brought into solution by treatment with a very small quantity of hydrofluoric acid. The solution, which usually amounted to about 250 c.c., was transferred to a 500 c.c. distillation flask, which was then sealed. The flask was put aside for one month to allow the emanation to attain a maximum. At the end of this period, the flask was opened, and the emanation boiled off, collected over hot water, dried, and introduced into an evacuated emanation electroscope in the manner described by Eve and McIntosh (*Phil. Mag.*, 1907, [vi], **14**, 234).

The chemicals were tested for radioactive matter and gave negative results.

The electroscope was standardised by means of a solution of radium prepared by dissolving a quantity of Joachimstahl pitchblende, containing 59·4 per cent. of uranium, and diluting until 250 c.c. of the solution contained $2{\cdot}02 \times 10^{-12}$ gram of radium. The radium content was calculated from the percentage of uranium by means of the "Rutherford-Boltwood" ratio, $3{\cdot}4 \times 10^{-7}$.

The normal leak of the electroscope was frequently determined, and between successive observations air was drawn through the electroscope for twelve hours to remove any radioactive matter.

The results of the tests are given in Table IX, together with the ultimate compositions of the samples of coal.

Table IX.

The Radium Contents and Ultimate Compositions of Coals.

Coal Field:	Leicestershire.	Derbyshire.	Lancashire.	Lancashire.	South Wales.
Class:	Non-coking.	Non-coking.	Cannel.	Cannel.	Anthracite.
C per cent.	76·44	78·48	79·55	82·07	88·41
H	4·90	5·71	5·81	6·15	3·41
N	1·53	0·93	1·19	1·54	1·04
S	0·83	0·79	0·96	1·48	1·27
Ash	2·52	1·38	5·17	2·38	3·85
O	13·78	12·71	7·32	6·38	2·02
Total	100·00	100·00	100·00	100·00	100·00
Radium per gram of ash	$2{\cdot}66 \times 10^{-12}$	$3{\cdot}91 \times 10^{-12}$	$1{\cdot}28 \times 10^{-12}$	$0{\cdot}042 \times 10^{-12}$	$0{\cdot}78 \times 10^{-12}$
Radium per gram of coal.	$0{\cdot}067 \times 10^{-12}$	$0{\cdot}054 \times 10^{-12}$	$0{\cdot}066 \times 10^{-12}$	$0{\cdot}001 \times 10^{-12}$	$0{\cdot}030 \times 10^{-12}$

The author's thanks are due to Mr. F. G. Atherton for his assistance in obtaining and analysing the three samples from the Lancashire Seam.

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[*Received, November 4th, 1921.*]

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[With Frederick William Smith].

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C per cent.	76·44	78·48	79·55	82·07	88·41
H	4·90	5·71	5·81	6·15	3·41
N	1·53	0·93	1·19	1·54	1·04
S	0·83	0·79	0·96	1·48	1·27
Ash	2·52	1·38	5·17	2·38	3·85
O	13·78	12·71	7·32	6·38	2·02
Total	100·00	100·00	100·00	100·00	100·00
Radium per gram of ash	$2·66 \times 10^{-12}$	$3·91 \times 10^{-12}$	$1·28 \times 10^{-12}$	$0·042 \times 10^{-12}$	$0·78 \times 10^{-12}$
Radium per gram of coal.	$0·067 \times 10^{-12}$	$0·054 \times 10^{-12}$	$0·066 \times 10^{-12}$	$0·001 \times 10^{-12}$	$0·030 \times 10^{-12}$

The author's thanks are due to Mr. F. G. Atherton for his assistance in obtaining and analysing the three samples from the Lancashire Seam.

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XXVIII.—*The Peroxidic Compounds of Copper.*

By (MISS) JOAN ALDRIDGE and MALCOLM PERCIVAL APPLEBEY.

PEROXIDIC compounds of copper of two distinct types have been described by several investigators, a series of yellowish-brown to olive-green precipitates of neutral character obtained by the action of hydrogen peroxide on cupric hydroxide, and a number of so-called cuprates of the alkalis and alkaline earths obtained by the oxidation of alkaline suspensions of cupric hydroxide by means of chlorine and presumably containing a higher oxide of copper with acidic properties. Preparations of the former class probably all consist of mixtures in varying proportions of cupric oxide and hydroxide with a yellow, gelatinous peroxide of formula CuO_2, as has been shown by the work of Osborne (*Amer. J. Sci.*, 1886, [iii], 32, 334), Moser (*Z. anorg. Chem.*, 1907, **54**, 121), and E. Müller (*ibid.*, 1907, **54**, 418). The analytical results of these investigators,

whilst approximating in many instances to the formula ascribed to the peroxide, always showed a deficiency of peroxidic oxygen. This deficiency might be due either to the instability of the compound or to the inclusion of unaltered cupric hydroxide. In view of the latter possibility, it was considered desirable to attempt the preparation by other methods, using as the starting material, not a solid compound of copper like the hydroxide, but a solution. Neither solutions of simple copper salts nor strongly alkaline solutions such as Fehling's solution, ammoniacal solutions, or the colloidal suspension of copper hydroxide in sodium hydroxide described by Justin-Mueller (*Compt. rend.*, 1918, **167**, 779) could be used, since no precipitate is produced by hydrogen peroxide in solutions of simple salts, whilst the presence of large concentrations of hydroxyl ion leads to the rapid decomposition of the compound. It seemed probable that the solutions of the double carbonate of sodium and copper, recently investigated by one of us (Applebey and Lane, T., 1918, **113**, 609), might prove suitable, since their alkalinity was very slight indeed. The investigation of this reaction was the primary object of the present experiments. In the course of the work, however, the effect of other oxidising agents on various copper solutions was tried, with the result that some further information has come to light with respect to reactions which had previously been studied by other workers. The experiments to be described fall into three sections:

(1) The action of hydrogen peroxide on carbonate solutions;

(2) The action of chlorine and of hypochlorite on Fehling's solution;

(3) The cuprates.

(1) *The Action of Hydrogen Peroxide on Carbonate Solutions.*

The solutions of sodium copper carbonate used in the preparations were made by adding to a solution saturated with sodium carbonate and bicarbonate at the room temperature varying quantities of dilute copper acetate solution with constant stirring. Such solutions are comparatively stable, but deposit the crystalline double carbonate on standing over-night if they contain more than 0·15 gram of copper per litre. It was found that any such solution, when treated in the cold with hydrogen peroxide, gave immediately a precipitate of the peroxide of a yellowish-brown colour, the greater part of the copper being removed from solution in this form. The precipitate is, however, not only unstable, but also very gelatinous, so that the preparation of a specimen for analysis presents great difficulties. All ordinary methods of filtration failed

to give a sufficiently rapid separation from the mother-liquor; the best results were obtained after many failures by the use of a filter-bed of powdered and graded glass contained in a Gooch crucible to which a light suction was applied. Such a device only retains the larger particles of the suspended gelatinous solid, but has the advantage of working very quickly. The precipitate collected in this filter was thoroughly washed with ice-cold water and analysed by dissolving it on the filter in a known amount of standard ferrous sulphate solution acidified with sulphuric acid. Estimation of the ferrous ion remaining and of the copper in the solution gave the required ratio of copper to peroxidic oxygen. The results obtained were very variable and gave clear evidence of the occurrence of rapid decomposition of the peroxide during the necessary manipulations. The most highly oxidised products were obtained by the use of excess of hydrogen peroxide at a low temperature. They contained more oxygen than corresponds with the formula Cu_2O_3, but never reached an oxygen content corresponding with CuO_2. Variation in the concentration of copper in the original solution had little influence on the composition of the precipitate except that there was always noticeable an increase in peroxidic oxygen as the quantity of precipitate to be dealt with diminished. This is simply a consequence of the greater rapidity with which smaller quantities can be handled. These observations, together with the colour of the products, indicate that the pure peroxide is produced by the reaction studied, but suggest that even the small concentration of free alkali present in the solutions reduces the stability to a degree which, combined with the intractable character of the precipitate, renders its separation in the pure state practically impossible.

(2) *The Action of Chlorine and of Hypochlorite on Fehling's Solution.*

When chlorine is passed through or hypochlorite solution added to Fehling's solution, a curious reaction occurs leading to the reduction of the solution with the precipitation of yellow to orange-red cuprous oxide. This reaction, which was first observed by Millon (*Compt. rend.*, 1862, **55**, 513), was attributed by him to the oxidation of the tartrate by the chlorine, with the formation of a reducing agent. The explanation is probably correct, although little can be said about the exact identification of the reducing agent.

Many experiments have been devised by the authors with the view of separating and identifying the unknown intermediate product. The passage of chlorine through strong solutions of Rochelle salt leads to oxidation with evolution of carbon dioxide,

but no products other than sodium carbonate could be separated from the solutions,* although slight reducing properties (to Fehling's solution) could be detected in partly oxidised solutions. It is therefore clear that the intermediate product, as would be expected from its reducing properties, is very rapidly destroyed by chlorine and does not accumulate in the solution. The only clue to its nature is the formation of a faint violet coloration on addition of ferric chloride to such solutions, similar in appearance to the coloration produced by the same reagent in presence of dihydroxymaleic acid, which Fenton has shown to be a product of the oxidation of tartaric acid by hydrogen peroxide. The reaction with sodium hypochlorite is similar but more vigorous, a great evolution of heat and violent liberation of carbon dioxide taking place when strong hypochlorite is employed.

The authors are unable to confirm the statement made by Millon (*loc. cit.*) that the precipitate formed in the early stages of the reaction of hypochlorites with Fehling's solution differs in any essential particular from that produced in the later stages. Millon states that the product first obtained with calcium hypochlorite is pale yellow and shows the reactions of "a double salt of calcium carbonate and cuprous formate." Exactly what analytical reactions were used by Millon is not stated, but the authors have convinced themselves by repeated tests that no trace of carbon dioxide is evolved from the properly washed precipitate with dilute acids, and concentrated sulphuric acid gives no carbon monoxide. There is no doubt that the precipitate is simply the finely divided form of cuprous oxide which frequently occurs in the early stages of reduction of Fehling's solution and that Millon's statement arose from inclusion in the precipitate of mother-liquor containing tartrate and carbonate. It may perhaps be added that the precipitate bears no resemblance in appearance or reactions to the colourless cuprous formate described by Angel (T., 1906, **89**, 345).

In the course of the experiments on the action of hypochlorite on Fehling's solution a somewhat remarkable time-reaction has been observed, the further examination of which may possibly throw some light on the course of the reactions involved. When a small quantity of strong hypochlorite is added to Fehling's solution, the precipitate of cuprous oxide does not appear immediately but only after the lapse of about half a minute. If a further small quantity of hypochlorite be now added, the first effect is to produce complete and rapid re-solution of the precipitate present; only after another period of waiting the precipitate reappears. This may be repeated

* Potassium hydrogen tartrate crystallises out during the chlorination owing to the hydrochloric acid formed in the oxidation.

many times, the precipitate dissolving after each addition of hypochlorite and coming down again after a short time. The reaction produces heat, and the times necessary for precipitation after each addition gradually diminish owing to the rise in temperature, unless precautions are taken. Presumably the changes described are to be explained as follows. The first effect of each addition of hypochlorite is to oxidise the cuprous oxide to cupric oxide, which dissolves in the excess of tartrate present in the Fehling's solution. The remainder of the hypochlorite then reacts with tartrate, forming the unknown reducing agent and therefore causing a further precipitation of cuprous oxide. The comparative slowness of the latter change enables the two stages of the reaction to be observed.

(3) *The Cuprates.*

Krüger (*Pogg. Ann.*, 1844, **62**, 445) first observed the formation by the chlorination of alkaline suspensions of cupric hydroxide of pink solutions which he supposed to contain salts of an acidic peroxide of copper. Other investigators have failed to repeat the preparation, so that Krüger's cuprates have been regarded with some suspicion. In the course of the present work we have occasionally obtained similar pink solutions by the chlorination of solutions of sodium copper carbonate, and the examination of the conditions of reaction has led us to the view that Krüger's cuprates are simply dilute solutions of permanganate produced by traces of manganese present as impurity in the solutions. The grounds for this view are as follows:

(*a*) When materials free from manganese and chlorine from a cylinder are used, the pink colour never appears.

(*b*) When chlorine prepared from manganese dioxide is used, the colour is obtained, but not if an efficient wash-bottle is used.

(*c*) The addition of a small trace of manganese salt to the solution to be chlorinated ensures the formation of the colour.

(*d*) The absorption spectrum of the pink solutions is identical in every respect with that of a permanganate solution of similar tint.

(*e*) The pink colour is obtained equally well or even better if the solution contains no copper at all, provided that the necessary trace of manganese is present.

All the above statements have been verified in respect to the solutions obtained from alkaline suspensions of cupric hydroxide as well as in respect to the chlorination products of the double carbonate solutions, and leave no doubt that the so-called cuprates of the alkalis have no real existence.

The cuprates of the alkaline earths, which have been described

by Krüger (*loc. cit.*), Crum (*Annalen*, 1845, **55**, 213), and Osborne (*loc. cit.*), are insoluble substances produced by the addition of dilute solutions of copper salts to a suspension of bleaching powder. The precise formulæ and compositions of these reddish-purple precipitates have never been satisfactorily settled, since all preparations undoubtedly contain unchanged bleaching powder, but it is interesting to note that they are obtained even when bleaching powder prepared from pure calcium oxide and cylinder chlorine is used. They are therefore real substances and are not, like the alkali compounds of Krüger, due to impurities.

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XXIX.—*The Velocity of Reaction in Mixed Solvents. Part II. The Velocity of Saponification of the Ethyl Esters of some Monosubstituted Benzoic Acids.*

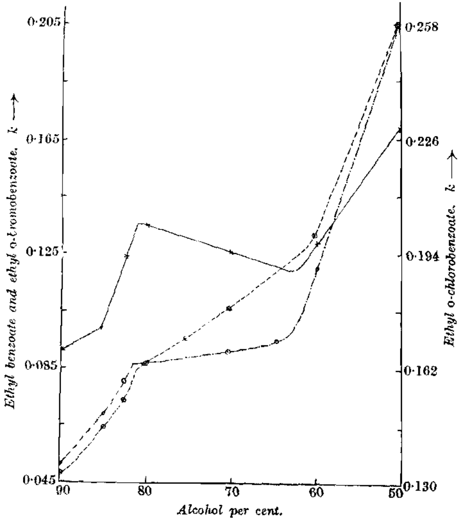
By ALBERT ERIC CASHMORE, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH.

IN Part I of this series (T., 1921, **119**, 970) a study was made of the reaction between the ethyl ester of a typical aromatic acid and a typical aliphatic acid and potassium hydroxide in a binary solvent medium consisting of ethyl alcohol and water. The results showed that, even with esters of such widely differing types as ethyl benzoate and ethyl *iso*butyrate, the character of the curve showing the relation between the value of the velocity constant *k* and the percentage composition of the medium is the same. In each case the curve was divisible into four phases, and in each phase the relation between *k* and the composition of the medium was found to be linear. Finally, the change from one phase to the next occurred at such compositions of the solvent medium that molecular complexes between the alcohol and water seemed to be indicated.

The work has now been extended to include the ethyl esters of monosubstituted benzoic acids, in order to ascertain whether the generalisations drawn from our results are without exception. In the first place ethyl *o*-bromobenzoate, ethyl *p*-chlorobenzoate, and ethyl *p*-toluate were selected, and it was noticed that with the first ester abnormal results were obtained when the solvent medium contained from 85 to 60 per cent. of alcohol. The velocities of saponification of ethyl *o*-chlorobenzoate, ethyl *o*-iodobenzoate, and ethyl *m*-toluate were therefore determined under the same conditions

to see if the cause of the anomaly was connected in any way with the position of the substituent in the benzene nucleus. The ethyl esters of *ortho*-substituted benzoic acids were found to be abnormal, and an attempt was made to include ethyl *o*-toluate in the series, but the reaction velocity was found to change so slowly with small

FIG. 1.



——— *Ethyl* o-*bromobenzoate.* —·—·— *Ethyl* o-*chlorobenzoate.*
— — — — *Ethyl benzoate.*

changes in the composition of the medium and, further, the values of k were themselves so small that the results merely served to indicate that the behaviour of this ester was similar to that of other ethyl esters of *ortho*-substituted benzoic acids.

The investigation is now being continued in three directions:

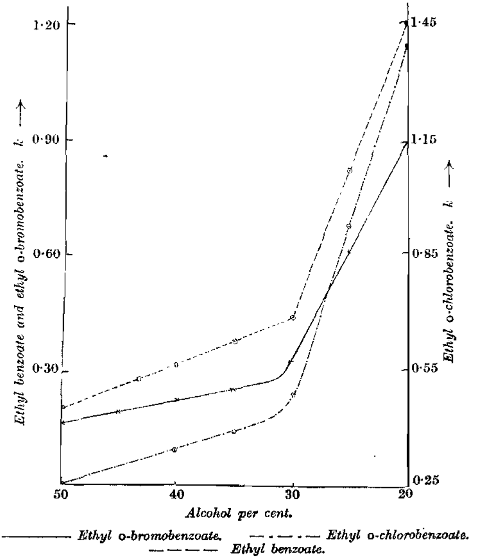
(*a*) The influence of the acid in the case of the ethyl esters of monobasic aliphatic acids.

(*b*) The effect due to a change of alkali hydroxide.
(*c*) The effect of variation of temperature.

Theoretical.

A consideration of the results given in Tables X—XV shows, as was to be expected, that the value of k, calculated from the

Fig. 2.



equation for a bimolecular reaction, is constant over the range of the reaction examined.

The ratio $k_{\text{ethyl isobutyrate}}/k_{\text{ethyl benzoate}}$ was found to have a nearly constant value (*loc. cit.*), but if the ratio $k_{\text{ester}}/k_{\text{ethyl benzoate}}$ be calculated for any one of the esters examined, it will be found that this ratio tends to decrease as the percentage of alcohol

in the solvent is decreased. The esters of the *ortho*-substituted benzoic acids behave in exactly the same way if we exclude those values of *k* which are abnormal. The decrease in the value of the ratio is very marked in the case of ethyl *p*-chlorobenzoate, and appears to be, to some extent, a function of the solubility of the ester in the solvent.

TABLE I.

k (Ethyl benzoate = 1).

Per cent. alcohol.	*o*-Chloro-benzoate.	*o*-Bromo-benzoate.	*o*-Iodo-benzoate.	*p*-Chloro-benzoate.	*m*-Toluate.	*p*-Toluate.
95	3·43	2·32	1·40	4·25	0·88	0·48
90	2·34	1·87	1·09	4·17	0·88	0·47
85	2·40	1·57	1·01	4·18	0·80	0·47
80	1·90	1·59	0·79	4·23	0·68	0·46
70	1·55	1·17	0·64	4·06	0·77	0·42
60	1·43	0·98	0·58	3·91	0·66	0·43
50	1·25	0·82	0·44	—	0·61	0·36
40	1·15	0·75	0·42	2·90	0·56	0·39
35	1·13	0·73	0·45	2·82	0·60	—
30	1·22	0·76	0·58	3·53	0·75	0·40
25	1·12	0·74	—	2·60	0·71	0·41
20	1·15	0·74	—	—	0·70	—

A study of the curve, connecting *k* with the composition of the solvent, for any one ester shows that we are dealing with a reaction passing through a succession of four phases, in each of which the relation between *k* and the composition of the medium is linear. The abnormal results obtained in the case of the esters of the *ortho*-substituted benzoic acids do not appear to affect this generalisation in any way. The observed values of *k* and those calculated for a linear relationship are tabulated for two typical esters, ethyl *p*-toluate and ethyl *o*-chlorobenzoate.

TABLE II.

Per cent. alcohol.	Ethyl *p*-toluate. *k* (obs.).	Ethyl *p*-toluate. *k* (calc.).	Ethyl *o*-chlorobenzoate. *k* (obs.).	Ethyl *o*-chlorobenzoate. *k* (calc.).
95	0·0134	0·0137	0·098	0·102
90	0·0230	0·0224	0·134	0·127
85	0·0310	0·0310	0·152	0·151
82·5	0·0355	0·0355	0·160	0·163
80	0·036	0·035	0·162	0·161
70	0·045	0·046	0·164	0·167
65	—	—	0·173	0·171
60	0·058	0·055	0·190	0·190
50	0·075	0·081	0·258	0·260
45	0·092	0·094	—	—
40	0·113	0·107	0·332	0·331
35			0·400	0·380
30			0·52	0·51
25			0·92	0·95
20			1·40	[illegible]

The critical points were determined by calculating the points of intersection of the phases and were found to agree with those obtained in the case of ethyl benzoate and ethyl *iso*butyrate. The first critical point was found to occur at 80·7 per cent. alcohol, as an average value for the esters examined. The second critical point gave two very sharply-defined values, depending apparently on the nature of the ester; the mean value for the ethyl esters of *ortho*-substituted benzoic acids was found to be 62·5 per cent. alcohol, whilst for the other esters the mean value was 59·5 per cent. alcohol. It was not easy to determine this critical point, as the change in direction from one phase to the next is slight and consequently small errors in the value of k might be a possible explanation of the two values of the critical point. On the other hand, between 56 and 62·5 per cent. of alcohol no fewer than three simple alcohol–water complexes are possible.

The third critical point occurred at a mean value of 31 per cent. alcohol, and there was a period of transition between 31 and 35 per cent. alcohol.

TABLE IIIa.

Ester.	Critical points (per cent. alcohol).		
Ethyl *o*-chlorobenzoate	80·7	62·5	31·0
,, *o*-bromobenzoate	,,	,,	30·6
,, *o*-iodobenzoate	,,	,,	—
,, *p*-chlorobenzoate	80·5	58·5	—
,, *m*-toluate	80·8	60·0	31·0
,, *p*-toluate	80·5	59·0	—

In the case of those esters which were too insoluble in a solvent containing 20 per cent. alcohol for determinations of the velocity constant to be possible, an accurate calculation of the third critical point could not be made, as the fourth phase was defined by only two points.

It seems scarcely possible that the critical points could agree so closely with the values required for the formation of simple complexes between alcohol and water, in the case of eight esters, unless these complexes do actually exist.

TABLE IIIb.

Complex.	Per cent. alcohol. Calculated.	Observed.
$5C_2H_5\cdot OH,3H_2O$	81	80·7
$2C_2H_5\cdot OH,3H_2O$	63	62·5
$3C_2H_5\cdot OH,5H_2O$	60·5	59·7
$C_2H_5\cdot OH,2H_2O$	56·1	—
$C_2H_5\cdot OH,6H_2O$	29·9	30·7

If we consider any one phase and calculate for a number of points on that phase the weight of water in 100 grams of solvent

above the amount required for a possible complex formation and then plot these quantities against the corresponding values of *k*, the relation will be found to be linear.

The accelerative effect due to the added water varies from phase to phase; but it is a most striking fact that in the case of the ethyl esters of the *ortho*-substituted benzoic acids we have a phase, in which the composition of the solvent changes from 80·7 per cent. of alcohol to 62·5 per cent. of alcohol, where the value of *k* is constant, within the limits of experimental error, throughout the phase. In one case, the value of *k* falls as the percentage of water in the phase increases, and in another case some evidence points to a similar phenomenon. These results were so abnormal that the experiments were repeated many times and it appeared as if two values of *k* were possible in the case of these esters for any one solvent in this phase (Tables XIV and XV).

The esters of *meta*- and *para*-substituted benzoic acids behave in the same manner as ethyl benzoate, in that the accelerative influence of added water is always positive and that the critical points agree with those obtained for ethyl benzoate.

EXPERIMENTAL.

The ethyl alcohol was rectified and the ethyl alcohol–water mixtures prepared in the manner described in Part I (*loc. cit.*).

The substituted benzoic acids were prepared by the usual methods. *o*-Chloro-, *o*-bromo-, and *o*-iodobenzoic acids were prepared from commercial anthranilic acid, *p*-chlorobenzoic and *p*-toluic acids were prepared from commercial *p*-toluidine, and the *m*-toluic acid was a Kahlbaum preparation. The acids were all recrystallised from aqueous alcohol until the required melting points were obtained.

The ethyl esters of these acids were prepared and purified in the manner described for ethyl benzoate.

The hydrochloric acid solutions employed in the titrations and the solutions of potassium hydroxide in the alcohol–water mixtures were prepared as previously described.

The experiments were carried out at 30° in the manner described in Part I.

In some cases considerable difficulty was experienced in obtaining even a *N*/400-solution of the ester in alcohol–water mixtures containing less than 30 per cent. of alcohol. The ester appears to form a very fine suspension in the alcohol–water mixture and true solution was only to be detected by the regularity of the velocity constant.

The results are shown in the following tables and curves, all of which are the result of duplicate or triplicate experiments.

Table IV.

Ethyl *o*-chlorobenzoate (b. p. 122°/15 mm.).

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·06189	0·02222	0·096—0·099	0·098
90	0·05165	,,	0·120—0·139	0·134
85	0·05695	,,	0·148—0·153	0·152
82·5	0·05551	,,	0·156—0·164	0·160
80	0·05085	,,	0·158—0·164	0·162
70	0·04714	,,	0·160—0·167	0·164
65	0·04610	,,	0·169—0·176	0·173
60	0·04849	,,	0·184—0·195	0·190
50	0·05071	0·01666	0·249—0·270	0·258
40	0·04240	,,	0·321—0·338	0·332
35	0·02055	0·01111	0·39 —0·41	0·40
30	0·01344	0·00666	0·51 —0·53	0·52
25	0·00553	0·00226	0·90 —0·93	0·92
20	0·00532	,,	1·34 —1·51	1·40

Table V.

Ethyl *o*-bromobenzoate (b. p. 135°/15 mm.).

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·07112	0·02222	0·0645—0·0655	0·065
90	0·05390	,,	0·091 —0·0925	0·091
85	0·05224	,,	0·094 —0·108	0·100
82·5	0·05662	,,	0·120 —0·128	0·124
80	0·06090	,,	0·130 —0·140	0·135
70	0·06423	,,	0·117 —0·127	0·124
65	0·04610	,,	0·116 —0·124	0·122
60	0·05214	,,	0·123 —0·135	0·130
50	0·04300	,,	0·160 —0·171	0·168
45	0·04164	0·01666	0·185 —0·195	0·190
40	0·03945	,,	0·207 —0·227	0·218
35	0·04283	0·01333	0·245 —0·271	0·260
30	0·04121	0·01111	0·315 —0·328	0·323
25	0·00553	0·00226	0·58 —0·63	0·61
20	0·00532	,,	0·89 —0·93	0·91

Table VI.

Ethyl *o*-iodobenzoate (b. p. 148°/15 mm.).

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·06189	0·02222	0·038—0·040	0·039
90	0·05165	,,	0·051—0·055	0·053
85	0·05695	,,	0·061—0·068	0·064
82·5	0·05551	,,	0·063—0·070	0·067
80	0·05357	,,	0·064—0·070	0·067
70	0·04714	,,	0·066—0·072	0·068
65	0·04610	,,	0·071—0·074	0·073
60	0·04849	,,	0·074—0·080	0·077
50	0·04605	,,	0·090—0·093	0·091
40	0·04240	0·01575	0·118—0·127	0·121
35	0·02055	0·01111	0·154—0·170	0·161
30	0·01766	0·00667	0·239—0·252	0·246

Measurements in 25 per cent. alcohol and in 20 per cent. alcohol could not be carried out owing to the insolubility of the ester.

TABLE VII.

Ethyl *p*-chlorobenzoate (b. p. 118°/15 mm.).

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·02195	0·01111	0·113—0·125	0·119
90	0·02201	,,	0·196—0·206	0·202
85	0·02080	,,	0·258—0·275	0·266
82·5	0·02003	,,	0·320—0·335	0·33
80	0·02098	0·00833	0·35 —0·36	0·36
70	0·02211	0·01111	0·42 —0·44	0·43
60	0·01756	0·00833	0·50 —0·54	0·515
45	0·01687	,,	0·68 —0·74	0·71
40	0·01559	0·00667	0·83 —0·84	0·84
35	0·01653	0·00833	0·97 —1·03	1·00
30	0·01702	0·00741	1·46 —1·58	1·50
25	0·00483	0·00226	1·97 —2·27	2·13

Measurements in 20 per cent. alcohol could not be carried out owing to the insolubility of the ester.

TABLE VIII.

Ethyl *m*-toluate.

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·06189	0·02222	0·0235—0·0260	0·0245
90	0·05165	,,	0·036 —0·040	0·038
85	0·05695	,,	0·049 —0·054	0·052
82·5	0·05551	,,	0·054 —0·060	0·057
80	0·05085	,,	0·057 —0·061	0·058
70	0·05551	,,	0·069 —0·075	0·071
60	0·04849	,,	0·082 —0·090	0·087
50	0·04605	,,	0·120 —0·128	0·125
40	0·04240	0·01666	0·157 —0·175	0·164
35	0·02055	0·01111	0·207 —0·217	0·214
30	0·01766	0·00833	0·31 —0·33	0·32
25	0·00553	0·00226	0·55 —0·61	0·58
20	0·00483	,,	0·83 —0·89	0·86

TABLE IX.

Ethyl *p*-toluate.

Per cent. alcohol.	c_{KOH}.	c_{ester}.	Limit k.	k.
95	0·07112	0·03333	0·0129—0·0136	0·0134
90	0·05390	,,	0·022 —0·024	0·023
85	0·05224	,,	0·0295—0·0325	0·031
82·5	0·05665	,,	0·0345—0·036	0·0355
80	0·06090	,,	0·038 —0·0405	0·038
70	0·06423	,,	0·044 —0·047	0·045
60	0·05214	,,	0·055 —0·060	0·058
50	0·05893	,,	0·070 —0·079	0·074
45	0·04164	0·02222	0·090 —0·094	0·092
40	0·03945	,,	0·110 —0·120	0·113
30	0·04395	0·01111	0·20 —0·215	0·21
25	0·00506	0·00226	0·33 —0·35	0·33

Measurements in 20 per cent. alcohol could not be carried out owing to the insolubility of the ester.

TABLE X.

Ethyl *o*-iodobenzoate.
60 per cent. alcohol.
$a = 0\cdot04849$; $b = 0\cdot02222$
HCl = 0·02725 *N*.

Time (mins.).	*x*. 10.	*k*.
30	0·0229	0·077
130	0·0778	,,
175	0·0937	,,
205	0·1079	,,
235	0·1166	0·076
265	0·1256	0·077
295	0·1324	0·076
330	0·1387	0·074
370	0·1504	0·073
	Mean	0·076

Ester saponified = 67·7 per cent.

TABLE XI.

Ethyl *m*-toluate.
20 per cent. alcohol.
$a = 0\cdot02414$; $b = 0\cdot01130$.
HCl = 0·0084 *N*.

Time (mins.).	*x*. 10.	*k*.
30	0·0132	0·89
60	0·0238	0·86
90	0·0316	0·84
120	0·0415	0·86
150	0·0485	0·87
190	0·0554	0·85
230	0·0617	0·85
270	0·0690	0·87
310	0·0739	0·87
350	0·0784	0·86
	Mean	0·86

Ester saponified = 69·4 per cent.

TABLE XII.

Ethyl *p*-toluate.
50 per cent. alcohol.
$a = 0\cdot05893$; $b = 0\cdot03333$.
HCl = 0·02367 *N*.

Time (mins.).	*x*. 10.	*k*.
60	0·0779	0·080
85	0·0993	0·078
120	0·1229	0·073
145	0·1393	0·073
180	0·1578	0·076
205	0·1773	0·073
245	0·1986	0·079
285	0·2063	0·073
330	0·2170	0·074
400	0·2411	0·070
	Mean	0·074

Ester saponified = 72·3 per cent.

TABLE XIII.

Ethyl *p*-chlorobenzoate.
45 per cent. alcohol.
$a = 0\cdot01687$; $b = 0\cdot00833$.
HCl = 0·0084 *N*.

Time (mins.).	*x*. 10.	*k*.
10	0·0103	0·80
20	0·0168	0·78
30	0·0235	0·71
40	0·0289	0·70
50	0·0338	0·68
60	0·0387	0·71
75	0·0444	0·71
90	0·0495	0·71
105	0·0528	0·72
120	0·0578	0·74
	Mean	0·72

Ester saponified = 69·4 per cent.

TABLE XIV.

Ethyl *o*-chlorobenzoate.
80 per cent. alcohol.
$a = 0\cdot04849$; $b = 0\cdot02222$.
HCl = 0·02725 *N*.

Time (mins.).	*x*. 10.	*k*.
45	0·0698	0·187
60	0·0850	0·184
75	0·1006	0·190
90	0·1126	0·187
105	0·1212	0·186
150	0·1515	0·192
180	0·1605	0·188
220	0·1760	0·192
280	0·1896	0·192
	Mean	0·189

Ester saponified = 85·4 per cent.

Ethyl *o*-chlorobenzoate.
80 per cent. alcohol.
$a = 0\cdot05085$; $b = 0\cdot02222$.
HCl = 0·02725 *N*.

Time (mins.).	*x*. 10.	*k*.
45	0·0684	0·172
60	0·0801	0·161
80	0·0995	0·164
100	0·1129	0·161
120	0·1260	0·161
140	0·1363	0·159
170	0·1502	0·160
200	0·1603	0·158
240	0·1747	0·162
	Mean	0·162

Ester saponified = 78·6 per cent.

TABLE XV.

Ethyl *o*-bromobenzoate.
80 per cent. alcohol.
$a = 0{\cdot}04816$; $b = 0{\cdot}02222$.
HCl = 0·02725 *N*.

Time (mins.).	*x*. 10.	*k*.
50	0·0605	0·139
70	0·0771	0·139
90	0·0916	0·134
120	0·1100	0·137
150	0·1245	0·135
180	0·1386	0·137
210	0·1510	0·140
240	0·1597	0·139
310	0·1771	0·140
	Mean	0·138

Ester saponified = 79·8 per cent.

Ethyl *o*-bromobenzoate.
80 per cent. alcohol.
$a = 0{\cdot}05085$; $b = 0{\cdot}02222$.
HCl = 0·02725 *N*.

Time (mins.).	*x*. 10.	*k*.
50	0·0590	0·129
90	0·0918	0·129
120	0·1068	0·125
150	0·1221	0·122
170	0·1352	0·129
190	0·1420	0·127
210	0·1479	0·123
240	0·1583	0·127
275	0·1672	0·127
	Mean	0·127

Ester saponified = 75·2 per cent.

In Tables XIV and XV are shown two different values of *k* which were found for both the esters in 80 per cent. alcohol. The values were re-determined and again confirmed, with the result that the high value of *k* appears to be the correct one for ethyl *o*-bromobenzoate and the low value of *k* for ethyl *o*-chlorobenzoate. At this time a few experiments were being carried out on the influence of temperature, and in two experiments at 15° a value of *k* was obtained for ethyl *o*-chlorobenzoate which indicated, from the temperature coefficient, that the higher value of *k* at 30° was the correct one.

Summary.

(1) A study has been made of the influence of the composition of a binary solvent mixture on the velocity of reaction between potassium hydroxide and the ethyl ester of certain monosubstituted benzoic acids in ethyl alcohol–water mixtures.

(2) The curves showing the relation between the value of *k* and he percentage composition of the solvent are of the same general haracter for each of the esters examined. The curves show that ve are dealing with a process divisible into a succession of four hases, and the relation between the value of *k* and the composition f the solvent is linear for each phase.

(3) The critical points occur at compositions of the solvent which e in every case those demanded by simple complexes between hyl alcohol and water. The existence of such complexes seems be the simplest explanation of the phenomena observed.

(4) The slope of the curve for any ester compared with that for hyl benzoate seems to depend to some extent on the solubility that ester in the solvent, if less than 60 per cent. of alcohol be esent in the solvent.

(5) Certain abnormal results have been observed in the case of the ethyl esters of the *ortho*-substituted benzoic acids examined, but these results do not in any way affect the conclusions drawn.

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CHEMICAL LABORATORIES,
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XXX.—*Phenolcamphorein.*

By SRI KRISHNA.

COLLIE (T., 1893, **63**, 961) prepared a camphorfluorescein from camphoric anhydride and resorcinol; and obtained very poor yields of the compound. This result is due to the fact that the anhydride is destroyed under the conditions usually chosen in preparing compounds of this class. Phenolcamphorein may, however, be prepared under the regulated conditions described below.

Various condensing agents were employed for the preparation of this compound, and hydrogen chloride (T., 1921, **119**, 289) was found to be the most suitable, especially in presence of a small quantity of zinc chloride. The reaction was conducted at 95—100°; at 105—110° a brown product (probably a fluorone), very slightly soluble in alkalis, was obtained, and at higher temperatures (150°) the mixture soon changed to a black, tarry mass.

The phenolcamphorein and its various derivatives described in this paper are microcrystalline substances of very light colour, which deepens considerably on warming. The melting points of the compound and of its derivatives being low, drying was effected in a vacuum desiccator over sulphuric acid.

$$\textit{Phenolcamphorein},\ C_8H_{14}\!<\!\begin{matrix}C(C_6H_4\cdot OH)_2\\ \diamond\!\!>\!O\\ CO\end{matrix}$$

This substance was obtained by heating a mixture of 18 grams of camphoric anhydride, 22 grams of freshly distilled phenol, and 5 grams of finely powdered zinc chloride on a water-bath in a

current of dry hydrogen chloride for ten hours. The pink colour that developed after some time deepened towards the end of the reaction. The hot melt having been boiled with very dilute hydrochloric acid to remove zinc chloride, the residue was collected, washed, made into a paste with a little water, and poured into a litre of water containing 10 grams of sodium hydroxide. The solution was filtered after twelve hours and precipitated with dilute hydrochloric acid, and the chocolate-coloured precipitate, after being washed and dried, was freed from resinous impurities by the addition of boiling water to its alcoholic solution until a slight turbidity was formed. The mixture, having been boiled with animal charcoal and filtered, was treated with a dilute solution of sodium hydroxide, and the phenolcamphorein was precipitated with carbon dioxide. The salmon-coloured powder crystallised from alcohol as an orange-red, microcrystalline powder melting at 83° (Found: C = 75·33; H = 7·01. $C_{22}H_{24}O_4$ requires C = 75·00; H = 6·8 per cent.).

Phenolcamphorein dissolves in alkalis with ease, giving red solutions which change to a light yellow on neutralisation; its behaviour towards strong alkalis is similar to that of phenolcoumarein. It is soluble in alcohol or acetic acid, but insoluble in benzene or chloroform.

The *diacetyl* derivative, prepared in the usual way, the resinous products being separated as described above, was obtained as a pale yellow powder by precipitating the alcoholic solution with water, or as brown, microscopic crystals from acetic acid, melting at 59° (Found: C = 71·76; H = 6·29. $C_{26}H_{28}O_6$ requires C = 71·56; H = 6·42 per cent.).

The *dibenzoyl* derivative was prepared by the Schotten-Baumann method. The resinous products were separated by distillation in steam; the residue crystallised from alcohol in small, brown plates melting at 81—82° (Found: C = 77·42; H = 5·59. $C_{36}H_{32}O_6$ requires C = 77·14; H = 5·71 per cent.).

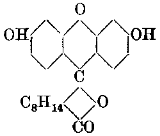
The *dimethyl* ether was prepared by heating on a water-bath for an hour an alkaline methyl-alcoholic solution of the camphorein with the calculated quantity of methyl sulphate. The cold mixture was faintly acidified, filtered, and precipitated with cold water. The resinous products were separated as already described, and on crystallisation from methyl alcohol the dimethyl ether was obtained as small, chocolate-coloured grains melting at 60° (Found: C = 75·96; H = 7·54. $C_{24}H_{28}O_4$ requires C = 75·79; H = 7·34 per cent.).

The *diethyl* ether, prepared in the usual way and purified by the method described above, crystallised from alcohol in very

small, orange crystals melting at 75° (Found : C = 76·22 ; H = 7·21. $C_{26}H_{32}O_4$ *requires C = 76·47 ; H = 7·84 per cent.).*

A *tetrabromo*-derivative was obtained by heating the camphorein and bromine in glacial acetic acid solution. The product, purified by precipitating the alcoholic solution with warm water, was, when dry, a pale yellow powder melting at 92° (Found : Br = 47·44. $C_{22}H_{20}O_4Br_4$ requires Br = 47·89 per cent.).

Resorcinolcamphorein,



This compound was prepared by heating a mixture of 10 grams of camphoric anhydride, 12 grams of resorcinol, and 8 grams of finely powdered zinc chloride at 120° for six hours in a current of dry hydrogen chloride. The product, isolated in the way described in the case of phenolcamphorein, was an orange-brown powder, but on purification the colour became slightly paler (compare Collie, *loc. cit.*).

Resorcinolcamphorein softens at about 180° and decomposes above 220°. It dissolves in alkali hydroxide solutions with a red colour which shows a strong, dirty green fluorescence. The solution in acetic acid is also fluorescent (Found : C = 72·79 ; H = 5·89. $C_{22}H_{22}O_5$ requires C = 72·23 ; H = 6·01 per cent.).

A *fluoran* derivative of camphoric anhydride was prepared by heating a mixture of 9 grams of camphoric anhydride and 8 grams of freshly distilled *p*-cresol for four hours at 120° in a current of dry hydrogen chloride. The melt was treated in the way described above, when a grey powder, melting at 55—57°, separated. It was almost insoluble in alkalis, and its solution in acetic acid exhibited a slight fluorescence (Found : C = 79·91 ; H = 7·01. $C_{24}H_{20}O_3$ requires C = 79·56 ; H = 7·18 per cent.).

In conclusion, I desire to express my thanks to Dr. F. G. Pope for his helpful suggestions and to the Research Fund Committee of the Chemical Society for the grant which defrayed part of the expenses incurred in this research.

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XXXI.—*Organo-derivatives of Thallium. Part IV. Action of Thallium Chlorides on the Grignard Reagent and on Organo-derivatives of Tin, Lead and Bismuth.*

By DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD.

MEYER and BERTHEIM (*Ber.*, 1904, **37**, 2051) attempted to obtain thallium diphenyl bromide by the action of thallic chloride on magnesium phenyl bromide, but failed to isolate any product pure for analysis. After considerable difficulty, the authors have obtained this compound in a pure state, and find it to be very sparingly soluble in organic solvents with the exception of pyridine, and to remain unmelted at 290°. In the tolyl series, *thallium di*-o-*tolyl chloride* and the *di*-p-*tolyl bromide* have also been isolated, these again showing extreme insolubility. The compound resulting from thallic chloride and magnesium α-naphthyl bromide, namely, *thallium di-α-naphthyl bromide*, melts at 272°, this agreeing with the authors' observation in previous work, that the heavier the grouping attached to the thallium atom, the lower the melting point of the resulting substance. Thallous bromide reacts with magnesium phenyl bromide, causing a quantitative reduction to metallic thallium. This reducing action of the Grignard reagent has also been noticed in the case of tellurium compounds (Lederer, *Ber.*, 1916, **49**, 1615). The reaction is all the more remarkable when compared with the behaviour of lead dichloride, which under the same conditions gives rise to lead tetraphenyl (Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1125). It was shown (Goddard, this vol., p. 39) that triphenylbismuthine and thallic chloride react in dry ether to produce diphenylchlorobismuthine and thallium diphenyl chloride. This reaction is now being extended to other organo-derivatives of the types: MR_3; MR_4; $R_3M{\cdot}Hal.$; $R_2MR'_2$; $R_3M{\cdot}Hal.$, and $R_3MR'{\cdot}Hal.$ Tin tetraethyl and thallic chloride in ether react according to the equation: $SnEt_4 + TlCl_3 = Et_2TlCl + Et_2SnCl_2$. If the solution containing the latter two substances be boiled with water, the thallium diethyl chloride will gradually disappear and thallous chloride be produced. The reaction with tin tetraphenyl is more complicated, and is best represented as follows:

(1) $3Ph_4Sn + 2TlCl_3 = 2Ph_2TlCl + 2Ph_3SnCl + Ph_2SnCl_2$

(2) $Ph_2SnCl_2 + H_2O = Ph_2Sn(OH)Cl + HCl$.

Indications of the presence of tin diphenyl chloride were traced, but Aronheim (*Annalen*, 1878, **194**, 154) showed that the compound

yields the hydroxychloride with water, and this probably accounts for the isolation of the latter compound. The reaction was carried out in xylene, no change taking place in alcoholic solution. Thallous chloride failed to react with tin tetraphenyl.

In the case of lead triethyl chloride, we have the following reaction :

(1) $Et_3PbCl + TlCl_3 = Et_2PbCl_2 + EtTlCl_2$

(2) $EtTlCl_2 = TlCl + EtCl.$

The assumption is made that under the conditions of experiment the unknown thallium ethyl dichloride is not stable, since only lead diethyl chloride and thallous chloride were isolated.

Thallic chloride and lead tetraphenyl react to give lead diphenyl chloride and thallium diphenyl chloride, this being equivalent to chlorination of the lead compound, and similar to the chlorination of triphenylstibine by thallic chloride (Goddard, *loc. cit.*). The difficulty of the separation of the two chlorides thus formed was overcome when it was observed that the unknown thallium diphenyl oxide or hydroxide is soluble in alcoholic potash, whereas the lead compound is insoluble.

Tri-*p*-tolylbismuthine gives rise to *thallium di*-p-*tolyl chloride* and a tervalent bismuth derivative, probably di-*p*-tolylchlorobismuthine. In the case of tri-α-naphthylbismuthine, the presence of di-α-naphthylchlorobismuthine was shown (Challenger and Allpress, T., 1921, **119**, 913) and *thallium di-α-naphthyl chloride* isolated.

Metallic thallium with lead tetraphenyl in xylene solution gave only small quantities of thallic hydroxide, no organic thallium compound being isolated.

Investigations on these double decompositions with other organometallic derivatives are proceeding.

EXPERIMENTAL.

Thallium Diphenyl Bromide.

To a solution of 23·8 grams of bromobenzene and 3·2 grams of magnesium ribbon in dry ether, 10·3 grams of thallic chloride in the same solvent were slowly added. The mixture was cooled in ice during the addition, and after the vigorous reaction had subsided, the product was heated on the water-bath for half an hour, cooled, and decomposed with water. After filtering, the dried residue was extracted with pyridine, when transparent, microscopic needles (2·5 grams) were obtained, which did not melt at 290°. These were treated with boiling acetic acid and recrystallised twice from pyridine before being pure for analysis (Found : Tl = 46·78 ; Br = 17·79.

$C_{12}H_{10}BrTl$ requires Tl = 46·58; Br = 18·25 per cent.). The compound is insoluble in alcohol, chloroform, benzene, acetone, light petroleum, acetic acid, or ethyl acetate.

*Thallium Di-*o*-tolyl Chloride.*

This compound was prepared by the addition of 4·8 grams of thallic chloride in dry ether to a solution of 10·0 grams of *o*-bromotoluene and 1·4 grams of magnesium in the same solvent. The reaction was carried out at room temperature, a vigorous effervescence taking place and a yellow solid separating, the mixture being allowed to stand for three days. After decomposition, the solid was extracted first with pyridine, then three times with boiling dilute hydrochloric acid and twice with boiling glacial acetic acid, finally with boiling pyridine. Slender, microscopic needles were obtained which did not melt at 290° (Found: Tl = 47·98; Cl = 8·32. $C_{14}H_{14}ClTl$ requires Tl = 48·39; Cl = 8·41 per cent.). The compound was insoluble in all organic solvents.

*Thallium Di-*p*-tolyl Bromide.*

The reaction was carried out with the same quantities as for the ortho-compound, but the Grignard solution was heated for an hour, and then decomposed on cooling, a greasy, yellowish-grey product being isolated. This was boiled for half an hour with 40 c.c. of pyridine, filtered, the solution evaporated to 7 c.c., and the bromide thrown out with ether. The substance was further washed with ether to remove the last traces of ditolyl, and then boiled with glacial acetic acid, when pale yellow needles were obtained (Found: Tl = 43·43; Br = 16·94. $C_{14}H_{14}BrTl$ requires Tl = 43·77; Br = 17·15 per cent.). The substance is insoluble in all organic solvents with the exception of pyridine.

Thallium Di-α-naphthyl Bromide.

To the solution of 33·6 grams of α-bromonaphthalene and 3·9 grams of magnesium in dry ether, 12·5 grams of thallic chloride in the same solvent were slowly added with vigorous shaking, the mixture being cooled in water. After the reaction had moderated, the whole was allowed to stand at room temperature for one hour, and then decomposed with water. The residue was taken up in pyridine, the solution on cooling depositing an oil. The latter solidified to a dark brown mass on the addition of water, and this was boiled with chloroform, the addition [illegible]

ng out a pale fawn solid. After filtering and washing with boiling chloroform until the washings were no longer coloured, the resulting compound melted at 272° (Found: Tl = 37·15; Br = 14·81. $C_{20}H_{14}BrTl$ requires Tl = 37·92; Br = 14·85 per cent.).

The compound is completely soluble in cold pyridine, moderately soluble in ethyl acetate, slightly soluble in alcohol, carbon tetrachloride, or glacial acetic acid, and insoluble in toluene.

Action of Thallous Bromide on Magnesium Phenyl Bromide.

To a solution prepared with 16·47 grams of bromobenzene and 2·52 grams of magnesium in dry ether, 25·2 grams of thallous bromide were added in small quantities, and the whole was boiled for seven hours and allowed to stand for a week. After decomposition, 18 grams of finely divided metallic thallium were obtained, and as the original thallous bromide should have yielded 17·8 grams, quantitative reduction had occurred.

Action of Thallic Chloride on (a) *Tin Tetraethyl* (b) *Tin Tetraphenyl.*

(*a*) To a solution of 2·75 grams of tin tetraethyl in 50 c.c. of ether, 3·6 grams of thallic chloride in 9 c.c. of the same solvent were added. A slight turbidity ensued and the whole was boiled for half an hour, when shining crystals separated together with a granular powder. The mixture was filtered hot and 1·35 grams of residue were obtained. This had an intolerable smell, and on treatment with water yielded thallium diethyl chloride and thallous chloride. The evaporated filtrate yielded a solid which softened appreciably at 84—85°, indicating the presence of tin diethyl chloride, and finally melted above 100°. On treatment with aqueous ammonia, thallic hydroxide was obtained and also a white solid which was prohahly tin diethyl oxide, but the quantity was not sufficient for further investigation.

(*b*) To a suspension of 3·0 grams of tin tetraphenyl in 30 c.c. of xylene, 3·32 grams of thallic chloride in 6 c.c. of ether were added. The mixture was boiled for half an hour, and a bulky, white solid separated, which was filtered after cooling, when 4·95 grams of a substance not melting at 260° were obtained. This was boiled with absolute alcohol and filtered hot, the residue (1·35 grams) being unchanged tin tetraphenyl (m. p. 221°). Evaporation of the alcoholic filtrate yielded 0·55 gram of thallium diphenyl chloride (Found: Tl = 52·09; Cl = 9·37. Calc., Tl = 51·84; Cl = 9·01 per cent.). The evaporation of the xylene filtrate gave three crops of crystals (*a*) 0·1 gram (m. p. 187°), which contained no thallium and was

identified with tin diphenyl hydroxychloride; (*b*) 0·3 gram (m. p. 99°), which was shaken with cold ether, the solution yielding 0·28 gram of tin triphenyl chloride (m. p. 206°); (*c*) 0·2 gram (m. p. 79°), which, after three crystallisations from light petroleum, softened at 42° and melted at 60°. This indicates a mixture of tin diphenyl chloride (m. p. 42°) and tin triphenyl chloride.

Action of Lead Triethyl Chloride on Thallic Chloride.

To a solution of 1·71 grams (1 mol.) of lead triethyl chloride (prepared by the action of dry hydrogen chloride gas on lead tetraethyl) in 50 c.c. of ether, 1·71 grams (1 mol.) of thallic chloride were added. The whole was boiled on the water-bath for one and a half hours and allowed to stand over-night, when pale yellow needles mixed with a granular compound separated (0·8 gram). Filtration and evaporation of the filtrate yielded a further 0·38 gram of the mixture. The combined solids were boiled for half an hour with absolute alcohol and filtered hot. The residue (0·4 gram) was white and was found to be thallous chloride (Found : Tl = 83·45. Calc., Tl = 85·19 per cent.). Evaporation of the alcohol yielded pale yellow needles (0·68 gram) which contained lead and were proved to be lead diethyl chloride (Found : Cl = 21·09. Calc., Cl = 21·09 per cent.).

Action of Thallic Chloride on Lead Tetraphenyl.

A mixture of 3·0 grams of lead tetraphenyl and 1·8 grams of thallic chloride in 60 c.c. of benzene was warmed on the water-bath for two hours. The residue obtained after filtering was boiled for half an hour with excess of alcoholic potash and filtered. The solid remaining (4·0 grams) was organic and contained lead, but no thallium, and by boiling with glacial acetic acid it yielded 1·6 grams of an inorganic lead compound. The alcoholic filtrate deposited long needles (1·7 grams) which did not melt at 270°, and these, on boiling with concentrated hydrochloric acid and crystallising from pyridine, gave pure thallium diphenyl chloride (Found : Cl = 8·95. Calc., Cl = 9·01 per cent.).

Action of Thallic Chloride on Tri-p-tolylbismuthine.

The solid obtained by shaking together 2·85 grams of tri-*p*-tolylbismuthine and 1·0 gram of thallic chloride in 50 c.c. of dry ether was filtered off after the mixture had stood half an hour. It was then boiled with acetone, and the filtrate gave a small quan-

tity of a tervalent bismuth compound, probably di-*p*-tolylchlorobismuthine, but the quantity was too small to manipulate. The residue from the acetone was recrystallised from pyridine, two crops of crystals being deposited; (*a*) consisting principally of inorganic bismuth and thallium salts (0·25 gram), (*b*) small, transparent needles of thallium di-*p*-tolyl chloride. The latter were purified by boiling with glacial acetic acid to remove any thallium *p*-tolyl dichloride and then recrystallised from pyridine (Found: Tl = 48·16; Cl = 8·53. $C_{14}H_{14}ClTl$ requires Tl = 48·39; Cl = 8·41 per cent.). *Thallium di-*p*-tolyl chloride* does not melt at 296° and is slightly soluble in alcohol or acetone, and insoluble in chloroform, light petroleum, toluene, or alcoholic ammonia.

Action of Thallic Chloride on Tri-α-naphthylbismuthine.

To 6·0 grams of tri-α-naphthylbismuthine in 60 c.c. of ether 1·91 grams of thallic chloride were added, and the whole was boiled for an hour and a half. From the cooled solution 6·2 grams of solid were obtained, and evaporation of the ether gave 0·2 gram of a grey mass which contained unchanged thallic chloride, bismuth oxychloride, and naphthalene. The 6·2 grams were boiled with benzene, the filtrate yielding 3·3 grams of unchanged bismuthine (m. p. 233—234°) and on evaporation 1·0 gram of a bismuth compound (m. p. 225°), which was found to be a mixture of tri-α-naphthylbismuthine and di-α-naphthylchlorobismuthine (m. p. 168°). The benzene residue (1·6 grams) was found to be *thallium di-α-naphthyl chloride* (Found: Tl = 42·47; Cl = 7·39. $C_{20}H_{14}ClTl$ requires Tl = 42·15; Cl = 7·35 per cent.). The compound is fairly soluble in hot pyridine, slightly soluble in glacial acetic acid, ethyl acetate, chloroform, or alcohol, and insoluble in ether, acetone, benzene, or carbon tetrachloride.

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XXXII.—*Metallic Derivatives of Nitrophenolic Compounds. Part IV. Some Complex Nitrophenoxide of Magnesium, Silver, and Lead.*

By ARCHIBALD EDWIN GODDARD and JAMES BERTRAM WARD.

IT has previously been shown (Goddard and Goddard, T., 1921 **119**, 2044) that the metals of the second vertical series of the periodic table readily yield salts with dinitrocresols. In the case of the mononitrophenols, however, magnesium is the only meta which easily gives compounds. Fritzsche (*Annalen*, 1859, **110**, 150) noted that "magnesia alba," when boiled with *o*-nitrophenol, does not all dissolve; no definite compound was isolated. The authors, however, using "light" magnesium carbonate, obtained the normal salt (+ H_2O) and its anhydrous derivative. A salt was formed from *m*-nitrophenol as described above, the solution evaporated to dryness, and the residue extracted with ether before drying, when a compound corresponding with the formula

$$Mg(OH)_2,Mg(OH)(C_6H_4O_3N),2H_2O$$

was isolated. This bears resemblance in structure to the oxychlorides of magnesium described by Bender (*Annalen*, 1871, **159**, 341). In the para-series, the complex derivative,

$$2(C_6H_4O_3N)_2Mg,C_6H_5O_3N,12H_2O,$$

was obtained, and from it the anhydrous normal salt, which on standing in air takes up water, forming the hydrate (+ $4H_2O$).

By treating an aqueous solution of *o*-nitrophenol with silver nitrate in the presence of a little ammonia, only the anhydrous salt was isolated. Fritzsche, using a slight excess of ammonia, had obtained the same compound. The composition of the para-salts depends on the conditions of preparation, the hydrate (+ H_2O) being formed by treating a cold solution of nitrophenol (1 mol.) and sodium hydrogen carbonate (1 mol.) with sodium hydroxide until neutral, and then adding silver nitrate (1 mol.). A mass of yellow needles was immediately precipitated, which, after standing for an hour, became orange. This colour change may be due to two forms of the salt or to the breaking down of a double silver ammonium salt first produced; in any case, the colour is not in accordance with that of para-salts. Another anomalous salt, $4C_6H_4O_3NAg,C_6H_5O_3N$, is obtained by adding a boiling solution of silver nitrate (1 mol.) to a boiling solution of ammonium *p*-nitrophenoxide containing an excess of ammonia, and allowing

the solution to cool from 70° to 20°, when deep scarlet needle of the above composition deposit. After these have been filtered off, the solution, on further cooling to 5°, gives greenish-yellow crystals of the double silver ammonium salt,

$$C_6H_4O_3NAg,C_6H_4O_3NNH_4,H_2O,$$

this becoming scarlet when heated. It is analogous to the double silver sodium thiosulphate described by Rosenheim and Steinhauser (*Z. anorg. Chem.*, 1900, **25**, 72). All these silver salts are completely soluble in pyridine, but insoluble in the usual organic solvents, with decomposition on heating. Fritzsche (*loc. cit.*) described the compounds $5C_6H_4O_3NAg,C_6H_5O_3N$ and

$$C_6H_4O_3NAg,C_6H_5O_3N,H_2O,$$

but the authors have not again isolated these.

In the case of lead compounds, the chief difficulty has been to obtain definite compounds and not mixtures; very slight changes in the mode of preparation appear to alter considerably the constitution of the salts. Fritzsche, by the addition of boiling lead acetate solution to sodium *p*-nitrophenoxide, obtained an orange precipitate having the composition $2PbO,3C_6H_4O_3NPb$, whilst hot lead acetate solution added to free *p*-nitrophenol solution gave $4C_6H_4O_3NPb,C_6H_5O_3N$.

The authors find that when *o*-nitrophenol is treated with a slight excess of ammonia, heated to boiling, and added to a warm solution of lead acetate ($+ 3H_2O$), the resulting precipitate has the composition $PbO,Pb(OH)(C_6H_4O_3N)$. By carrying out this process with *m*-nitrophenol, the compound $PbO,Pb(C_6H_4O_3N)_2$ was isolated, but if only warm solutions are used the salt obtained corresponds with the formula $2PbO,Pb(C_6H_4O_3N)_2,Pb(C_6H_4O_3N)(OH)$, which is comparable with the basic carbonates of Stromholm (*Z. anorg. Chem.*, 1904, **38**, 429). The previous salt, in general formula, resembles the lead sulphohaloids (Carnelly, T., 1876, **29**, 489; Parmentier, *Compt. rend.*, 1892, **114**, 298). In the para-series Fritzsche's compound, $4Pb(C_6H_4O_3N)_2,C_6H_5O_3N$, was isolated, warm solutions of the two components being used, but if the hot lead acetate solution was added to a hot, faintly ammoniacal solution of ammonium *p*-nitrophenoxide and the whole allowed to cool very slowly, the resulting salt had the composition $2Pb(C_6H_4O_3N)_2,C_6H_5O_3N$. By grinding the two components together in a mortar, and then boiling with water, the basic compound, $PbO,Pb(C_6H_4O_3N)_2$, was formed, whereas by using considerable excess of ammonia and warm solutions the more basic salt, $PbO,Pb(OH)(C_6H_4O_3N)$, was deposited. By pouring a solution of lead acetate into a very large excess of ammonia, a precipitate containing 83 per cent. of lead was obtained, and this,

when treated with *p*-nitrophenol in the hot, gave the compound $Pb(OH)_2,Pb(OH)(C_6H_4O_3N)$.

In the case of the nitrocresols, hot lead acetate solution was added to boiling, strongly ammoniacal solutions of the nitrocresols, and, in the cases of the 1 : 2 : 3-, 1 : 3 : 6-, and 1 : 4 : 3-nitrocresols, the composition of the lead derivative corresponded with $PbO,Pb(C_7H_6O_3N)_2$, but the 1 : 2 : 4-compound gave the substance $2PbO,Pb(C_7H_6O_3N)_2,Pb(OH)(C_7H_6O_3N)$, this being similar to the compound obtained from *m*-nitrophenol. The derivative of 2 : 4-dinitrophenol, $PbO,Pb(OH)(C_6H_3O_5N_2)$, resembled the salt from *o*-nitrophenol, and the dinitro-*o*-cresol gave the compound $PbO,2Pb(OH)(C_7H_5O_5N_2)$. Taken on the whole, all these lead salts are insoluble in water and the usual organic solvents, and exhibit the usual colour, with the exception of the *m*-nitrophenoxides, which are pale yellow instead of orange. Of the nitrocresol salts, all save the 1 : 2 : 4-compounds are decomposed by ethyl acetate with the production of lead acetate. These compounds may be said to fall principally under the three general headings : (I) PbO,PbR_2 or R·Pb·O·Pb·R, (II) PbO,Pb(OH)R or HO·Pb·O·Pb·R, and (III) $x PbR_2,RH$, where R is the aromatic residue. Formula (I) is analogous to the naturally occurring mineral " matlockite," and (II) to its substituted or basic form.

EXPERIMENTAL.

Derivatives of o-Nitrophenol.—$C_{12}H_8O_6N_2Mg,H_2O$, bright orange-red, crystalline plates, becoming deeper in colour in chloroform, carbon tetrachloride, light petroleum, or toluene, and giving yellow solutions in alcohol, acetone, or pyridine [Found : N = 8·82 (8·78); Mg = 7·80 (7·62); H_2O = 5·99 (5·65) per cent.]. $C_{12}H_8O_6N_2Mg$, light red. $C_6H_4O_3NAg$, brownish-red, glistening needles, decomposing with formation of silver oxide when boiled with alcohol, acetone, or toluene, and giving a yellow solution in pyridine [Found : Ag = 43·23 (43·87) per cent.]. $C_6H_5O_5NPb_2$, brownish-orange powder [Found : N = 2·27 (2·39) per cent.].

Derivatives of m-*Nitrophenol.*—$C_6H_7O_6NMg_2,2H_2O$, bright yellow, crystalline powder, becoming orange on boiling in pyridine, carbon tetrachloride, toluene, light petroleum, ether, or chloroform [Found : N = 5·62 (5·12); Mg = 17·93 (17·77) per cent.]. $C_{12}H_8O_7N_2Pb_2$, pale yellow, crystalline powder, darkening slightly in pyridine [Found : N = 3·56 (3·97); Pb = 59·09 (58·64) per cent.]. $C_{18}H_{13}O_{12}N_3Pb_4$, dull yellow powder, darkening slightly in toluene [Found : N = 3·17 (3·16); Pb = 62·92 (62·40) per cent.].

Derivatives of p-*Nitrophenol*.—$C_{24}H_{16}O_{12}N_4Mg_2,C_6H_5O_3N,12H_2O$, brilliant yellow plates, becoming paler on heating in acetone or toluene [Found: N = 7·48 (7·37); Mg = 5·05 (5·09); H_2O = 37·35 (37·17) per cent.]. $C_{12}H_8O_6N_2Mg$, darker yellow [Found: Mg = 8·03 (8·10) per cent.]. $C_{12}H_8O_6N_2Mg,4H_2O$, obtained by allowing the anhydrous compound to stand in the air [Found: Mg = 6·32 (6·53); H_2O = 19·34 (19·35) per cent.]. $C_6H_4O_3NAg,H_2O$, orange needles, decomposing slowly in the air and yielding silver oxide on boiling with most solvents. Its solutions in alcohol, acetone, or pyridine are greenish-yellow [Found: N = 5·32 (5·31); Ag = 40·50 (40·82); H_2O = 6·93 (6·82) per cent.]. $C_{24}H_{16}O_{12}N_4Ag_4,C_6H_5O_3N$, crimson, silky needles, becoming brown in alcohol, acetone, or toluene and giving a yellow solution in cold pyridine or water [Found: N = 6·16 (6·24); Ag = 38·29 (38·43) per cent.]. $C_6H_4O_3NAg,C_6H_8O_3N_2,H_2O$, greenish-yellow needles, becoming grey in alcohol or ethyl acetate, greyish-orange in acetone, orange-yellow in toluene or chloroform, and red in carbon tetrachloride [Found: N = 9·99, 9·88 (10·01); NH_4 = 4·07 (4·30); Ag = 25·66 (25·70); H_2O = 4·77 (4·20) per cent.]. $C_{48}H_{32}O_{24}N_8Pb_4,C_6H_5O_3N$, brilliant yellow needles, giving an orange solution in pyridine [Found: N = 6·05 (6·08); Pb = 39·67 (39·99) per cent.]. $C_{24}H_{16}O_{12}N_4Pb_2,C_6H_5O_3N$, dull yellow, blunt-ended needles [Found: N = 6·58 (6·34); Pb = 37·36 (37·49); $C_6H_5O_3N$ = 12·67 (12·58) per cent.]. $C_6H_7O_6NPb_2$, brilliant yellow, crystalline powder, which becomes slightly orange when heated in acetone [Found: N = 2·32 (2·32); Pb = 67·70, 68·15 (68·66) per cent.]. $C_{12}H_8O_7N_2Pb_2$, yellow powder [Found: Pb = 58·75 (58·64) per cent.]. $C_6H_5O_5NPb_2$, brilliant yellow powder [Found: N = 2·27 (2·39); Pb = 70·20 (70·76) per cent.].

Derivatives of Nitrocresols.—From 3-nitro-*o*-cresol, $C_{14}H_{12}O_7N_2Pb$, fine, bright red needles, partly soluble in pyridine and separating, on cooling, in pale pink crystals [Found: N = 3·57 (3·82); Pb = 55·56 (56·41) per cent.]. From 4-nitro-*o*-cresol,

$$C_{21}H_{19}O_{12}N_3Pb_4,$$

bright orange, crystalline powder, becoming pale red in pyridine [Found: N = 2·99 (3·15); Pb = 63·42 (62·11) per cent.]. From 6-nitro-*m*-cresol, $C_{14}H_{12}O_7N_2Pb$, bright yellow, crystalline powder [Found: N = 3·49 (3·82); Pb = 56·37 (56·41) per cent.]. From 3-nitro-*p*-cresol, $C_{14}H_{12}O_7N_2Pb$, orange-yellow powder, becoming deeper in colour in ethyl acetate, carbon tetrachloride, or pyridine [Found: N = 3·58 (3·82); Pb = 56·18 (56·41) per cent.]. From dinitro-*o*-cresol, $C_{14}H_{12}O_{11}N_4Pb_3$, orange-yellow, crystalline powder, becoming darker in toluene [Found: N = 5·22 (4·96); Pb = 55·02 (55·01) per cent.].

Derivative of 2 : 4-dinitrophenol, $C_6H_4O_7N_2Pb_2$, brilliant yellow, crystalline powder [Found : N = 4·53 (4·45); Pb = 65·07 (65·73) per cent.].

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XXXIII.—*A Critical Examination of the Aromatic Aldehydes occurring in certain Eucalyptus Oils.*

By ARTHUR RAMON PENFOLD.

DURING March, 1920, Mr. H. G. Smith and the author carried out an investigation on the aromatic aldehydes present in the oils of *Eucalyptus hemiphloia* and *E. polybractea*. The result of this work was the isolation of a hitherto unsuspected aldehyde named cryptal, as well as one closely resembling phellandral, whilst the presence of cuminaldehyde was confirmed. (This work is recorded in detail in Baker and Smith's 2nd edition of the "Eucalypts" [1920], pages 383—388.) Unfortunately, we were unable to separate any aromadendral, the aromatic aldehyde discovered by H. G. Smith in 1900 (see *J. Roy. Soc. New South Wales*, 1900, **34**, 286; also *Pharm. J.*, 1905, **75**, 356, 382; *Trans. Roy. Soc. South Australia*, 1916, **40**, 485). The purest specimens of cuminaldehyde isolated by us, however, possessed lævorotations varying from $-3{\cdot}6°$ to $-11{\cdot}8°$, which we believed to be due to aromadendral, but were unable to isolate it on that occasion.

In order to separate this lævorotatory aldehyde from the cuminaldehyde, and also to ascertain if the other aldehyde so closely resembling phellandral was in reality that particular aldehyde, the present author undertook the investigation about to be detailed. The result is that the aldehyde resembling phellandral has been isolated in a purer condition than before, and proved to be identical therewith, whilst an efficient and simple method has been found for separating cuminaldehyde in a state of purity from the accompanying lævorotatory one, which is shown to be phellandral.

The aldehyde "aromadendral," therefore, is merely a mixture of cuminaldehyde and phellandral, and this accounts for the absence of regularity in optical activity previously observed for preparations of this composite aldehyde, the lævorotation being dependent merely on the varying amount of phellandral present.

The author has been unable to detect the presence of any aldehyde

other than cuminaldehyde, phellandral, and cryptal, which three are now quite readily separated from each other.

They have been separated from various eucalyptus oils from three different States of the Commonwealth, and the optical activity of the two optically active ones has been found to be constant, namely: Phellandral, $\alpha = -130{\cdot}6°$ to $-131°$, whence $[\alpha]_D^{20°}$ $-138{\cdot}9°$. Cryptal, $\alpha = -76{\cdot}2°$, whence $[\alpha]_D^{20°}$ $-80{\cdot}75°$.

Experimental.

Aldehydes from E. hemiphloia, *N.S.W.*

Four hundred and sixty-two kilograms of the leaves and terminal branchlets of this species, procured from Cabramatta in the neighbourhood of Sydney during February, 1921, on distillation with steam yielded 2·3 kilos. of oil, equivalent to 0·5 per cent. A portion of the leaves of the young growth was kept separately from the greater bulk of the mixed young and old material.

The characters of the two oils were as follows:

	(1) Oil from young material.	(2) Oil from mixed material.
Density at 15°	0·8979	0·8902
Optical rotation	− 21·51°	− 28·02°
Refractive index at 20°	1·4889	1·4883
Cineole	trace only	trace only
Phellandrene	absent	present in moderate amount
Amount of oil	513 grams	964 grams

The oils were distilled at 760 mm., and the portions boiling above 185° reserved for treatment, No. 1 giving 200 c.c. and No. 2 400 c.c. of oil boiling above this temperature. Each of these fractions was shaken at intervals with 35 per cent. sodium hydrogen sulphite solution, and, after twenty-four hours, the emulsions were filtered with suction. The solid, crystalline cakes were washed with alcohol-ether until free from oil, and dried on porous plate. They weighed 35 grams and 65 grams respectively, and on treatment with sodium carbonate solution and steam distillation, 16 c.c. and 32 c.c. of aldehyde were obtained, which had the following characters:

	"Aromadendral."	
	Specimen "A" (16 c.c.).	Specimen "B" (32 c.c.).
Density at 15°	0·9682	0·9687
Optical rotation	− 47°	− 40°
Refractive index at 20°	1·5133	1·5144
M. p. of the oxime	84—85°	84°

Both the above samples of aldehyde, "A" and "B," were mixed, and reserved for subsequent treatment (see "aromadendral").

The filtrates from these were mixed and the aqueous hydrogen sulphite layer separated from the oil (see cryptal), the latter being again shaken with fresh 35 per cent. sodium hydrogen sulphite solution, when, after the lapse of twenty-four hours, a second crop of solid bisulphite compound was obtained, which was separated and purified, as described above. The amount obtained was 47 grams, and on treatment with sodium carbonate solution and steam distillation, 24 c.c. of aldehyde were obtained having the following constants:

Density at 15°	0·9487	Sample "C." Phellandral.
Optical rotation	− 129°	
Refractive index at 20°	1·4956	
M. p. of the oxime	87—88°	
M. p. of the acid obtained on oxidation	144—145°	

The aqueous hydrogen sulphite filtrate from the solid compound was separated from the oil, repeatedly washed with ether to remove traces of the latter, and decomposed with an aqueous solution of sodium hydroxide (the aldehyde is not regenerated with sodium carbonate), when 60 c.c. of crude cryptal were obtained.

After purification by means of neutral sodium sulphite solution in the cold, the aldehyde had the following constants:

Boiling point	98—100°	Sample "D." Cryptal.
Density at 20°	0·9442	
Optical rotation	− 76·2°	
Refractive index at 20°	1·4830	
M. p. of the semicarbazone	176—177°	

"*Aromadendral.*"—The mixed samples "A" and "B" were found to be identical with the aldehyde described under this name by Baker and Smith (*op. cit.*). After a number of trial experiments, the author was able to resolve this composite aldehyde into its components by the following procedure.

The mixed samples "A" and "B" were again treated with sodium hydrogen sulphite, and the crystalline compound was heated to boiling with a 35 per cent. solution of sodium hydrogen sulphite for about one hour. The mixture was kept over-night, and then filtered from the cuminaldehyde bisulphite compound which had crystallised out; the lævorotatory aldehyde was present in the filtrate as a soluble sulphonic acid. The solid compound was washed with 35 per cent. sodium hydrogen sulphite solution and on decomposition with sodium carbonate solution and steam distillation yielded cuminaldehyde of optical inactivity, whilst the

soluble sulphonic acid gave the lævorotatory aldehyde on treatment with sodium hydroxide solution. This aldehyde proved to be phellandral. As thus obtained, the aldehydes possessed the following constants :

	Cuminaldehyde.	Phellandral.
Boiling point	110°/10 mm.	90°/5 mm.
Density	0·982 at 15°	0·9412 at 20°
Optical rotation	inactive	— 130·85°
Refractive index at 20°	1·5287	1·4912
M. p. of the semicarbazone	210—211°	204—205°
,, ,, ,, hydrazone	126—127°	122—123°
,, ,, ,, oxime	—	87—88°
,, ,, ,, acid obtained by oxidation	—	144—145°

Sample " C," on rectification, yielded phellandral of the same chemical and physical characters as the above prepared sample.

To obtain confirmatory evidence of the accuracy of the method, a specimen of the original oil of *E. salubris* from West Australia distilled in 1904 was treated and the mixed aldehydes separated.

The constants of the composite aldehyde given by Baker and Smith, $d^{20°}$ 0·9534, $[\alpha]_D$ — 90·43°, $n^{20°}$ 1·5066, m. p. of the oxime 84—85°, pointed to its consisting largely of phellandral. On subjecting the mixed aldehydes to the treatment described under " aromadendral," pure cuminaldehyde and phellandral, $[\alpha]_D$ — 131·8°, were obtained.

The successful separation of the three aldehydes, cuminaldehyde, phellandral, and cryptal, depends on the use of pure sodium hydrogen sulphite, which was employed throughout the investigation, the ordinary commercial grade being untrustworthy.

Summary.

(1) A method has been devised for separating cuminaldehyde from phellandral when found occurring together.

(2) " Aromadendral " is shown to be a mixture of cuminaldehyde and phellandral in varying proportions.

(3) The three aromatic aldehydes, cuminaldehyde, phellandral, and cryptal, have been separated from each other in a state of purity when all three occur together, as they do in certain eucalyptus oils.

TECHNOLOGICAL MUSEUM, SYDNEY. [*Received, August 9th*, 1921.]

XXXIV.—*The Products of Nitration of Toluene.*

By WILLIAM HOWIESON GIBSON, REBECCA DUCKHAM, and RUTH FAIRBAIRN.

EARLY in 1915 it became necessary to accelerate and increase the output of trinitrotoluene used in filling high explosive shell, and on this account purification by crystallisation was abandoned, the crude product being substituted. In these circumstances it was found essential to study the nitration of toluene quantitatively at each stage, especially as little information could be obtained from the literature. One of us, therefore, outlined a programme of work designed to give the information desired on the proportions of mono-, di-, and tri-nitrotoluenes produced at each stage of manufacture and on the behaviour of the crude trinitrotoluene under varying temperature conditions. A summary of the results is now given, the method of thermal analysis being used throughout. The details of manipulation followed closely those of Philip (T., 1903, **83**, 814), and so are not further described.

Mononitration.

Previous workers are Holdermann (*Ber.*, 1906, **39**, 1256), Friswell (*J. Soc. Chem. Ind.*, 1908, **27**, 258), and van der Arend (*Verslagen K. Akad. Wetensch. Amsterdam*, 1908, 208).

Reference Curves.—As the product of mononitration is mainly *o*- and *p*-nitrotoluenes, the binary fusion curve for *o*- and *p*-nitrotoluenes was first plotted from the data given in Table I and Fig. 1.

TABLE I.

p-Nitrotoluene per cent.	Crystallisation point.	*p*-Nitrotoluene per cent.	Crystallisation point.
100	51·5°	50	16·7°
90	45·5	35	− 0·4
75	36·75	25	− 14·33
60	25·2	0	− 4

These values agree with results obtained by Holleman (*Rec. trav. chim.*, 1914, **33**, 1), which were not available at the time of our investigation. Bell and Spry (*J. Ind. Eng. Chem.*, 1921, **13**, 60) have since published similar figures.

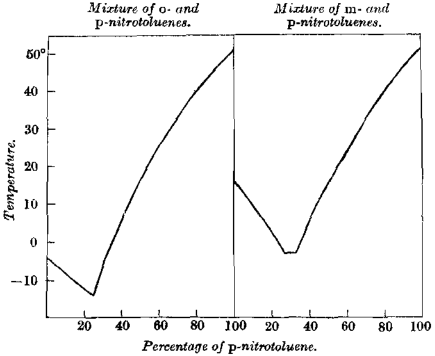
The fusion curve for *m*- and *p*-nitrotoluenes, not previously investigated, was plotted from the results given in Table II and Fig. 1.

TABLE II.

m-Nitrotoluene per cent.	Crystallisation point.	*m*-Nitrotoluene per cent.	Crystallisation point.
0	51·5°	73	−2·9°
25	36·2	75	−1·0
40	24·4	80	2·8
50	15·4	90	10·0
67	− 2·9	100	16·0

The ternary fusion diagram for *o*-, *m*-, and *p*-nitrotoluenes was partly studied, about thirty observations being made, chiefly in

FIG. 1.



the regions where small percentages of *m*-nitrotoluene are present. The results taken from this diagram and given in Table III were used in analysis.

TABLE III.

Addition of *m*-nitrotoluene to a mixture of 75 per cent. of *o*- and 25 per cent. of *p*-nitrotoluene.

m-Nitrotoluene per cent.	Crystallisation point.	*m*-Nitrotoluene per cent.	Crystallisation point.
1·03	− 15·3°	4·1	− 16·9°
2·04	− 15·9	5·08	− 17·4
2·93	− 16·3	8·85	− 19·3

Methods of Analysis.—I. *Special Method for Mononitrotoluene.*

When commercial nitrotoluene is cooled, the initial crystallisation point is rather difficult to determine, as it is not very far removed from the eutectic and there is a great risk of overcooling. The second crystallisation point is well defined, however, as the eutectic represents about 85 per cent. of the mixture.

The method adopted to obtain greater accuracy was to determine the second crystallisation point of the original mixture and then to add an equal quantity of pure *p*-nitrotoluene and determine the initial crystallisation point; as the mixture was quite rich in *p*-nitrotoluene, a well-defined halt was then obtained. The percentage of *p*-nitrotoluene P in this mixture is read off from the *o*-*p*-curve (Fig. 1), the small quantity of *m*-nitrotoluene present having, judging by the ternary diagram, much the same effect as the same quantity of o-nitrotoluene in depressing the crystallisation point. The percentage p of *p*-nitrotoluene in the mixture under investigation is consequently $p = 2(P - 50)$. The percentage m of *m*-nitrotoluene in the eutectic of the original mixture is read off from the curve drawn from Table III. Then, if x is the required percentage of *m*-nitrotoluene in the mixture and p the percentage of *p*-nitrotoluene,

$$x = 4m\,\frac{(100 - p)}{300 + m},$$

for in 100 parts of the mixture there are p parts of *p*-, x parts of *m*-, and $(100 - p - x)$ parts of *o*-nitrotoluene; the eutectic of this mixture, since the composition of the eutectic of *o*- and *p*-nitrotoluenes is 75 per cent. of *o*-nitrotoluene and 25 per cent. of *p*-nitrotoluene, will contain x parts of *m*-, $100 - p - x$ parts of *o*-, and $25/75\ (100 - p - x)$ parts of *p*-nitrotoluene, and the percentage of *m*-nitrotoluene in the eutectic is

$$m = \frac{100\,x}{\frac{4}{3}\,(100 - p - x) + x}.$$

II. *General Method Applicable to Ternary Mixtures.*

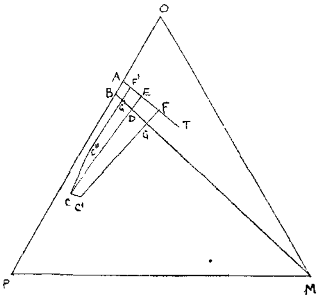
This depends on obtaining known and unknown mixtures of the same second crystallisation point.

In Fig. 2 a ternary composition diagram is shown, in which O, P, and M represent 100 per cent. of each of the isomerides in triangular co-ordinates, A represents the composition of the eutectic mixture of O and P, and T the ternary eutectic composition. B represents a known mixture of O and P, and

$B\,M$ a known curve of compositions obtained by adding M to B. The second crystallisation points of this series of mixtures are taken, corresponding with compositions along the boundary curve $A\,T$. Then let C represent any unknown mixture in the region $A\,P\,T$; its second crystallisation point E, corresponding with that of tbe known mixture D, is determined, a known percentage of M is added, and the new second crystallisation point F, corresponding with that of the known mixture G, is determined. The composition of the mixture C may then be calculated as follows:

Let x be the required percentage of O, and z the required percentage of M in the mixture C. Let h be the percentage of M added to 100 parts of C in the determination. Let d be the

FIG. 2.



percentage of M added to 100 parts of the known mixture B which gives the same second crystallisation point as C, and g the percentage of M added to 100 parts of B which gives the same second crystallisation point as C after the addition of h parts of M (d and g correspond with D and G in the diagram and are read off from the curve $B\,M$, plotted as second crystallisation point against added percentage of M). Also let p be the percentage of O in the mixture B.

Then $$\frac{x}{p} = \frac{z}{d} = \frac{z + h}{g}$$

hence $$z = \frac{d\,h}{g - d} \text{ and } x = \frac{p\,h}{g - d}.$$

The percentage of P in the mixture is $100 - x - z$.

If the substance M is not available for addition to the unknown mixture C, a definite percentage of the known mixture B may be added. Then, by similar reasoning, if x, z, p, and d have the same significance as before, but k is the percentage of O added to C when a quantity of mixture B is added for the second determination of the crystallisation point, and g the percentage of M added to 100 parts of B which gives the same second crystallisation point as the mixture formed by this addition of B to C,

$$\frac{z}{x} = \frac{d}{p} \text{ and } \frac{z}{x+k} = \frac{g}{p}.$$

hence

$$x = \frac{kg}{d-g} \text{ and } z = \frac{dkg}{p(d-g)}.$$

TABLE IV.

Curve *BM*.—The percentage of *m*-nitrotoluene added to a mixture of 70 per cent. of *o*- and 30 per cent. of *p*-nitrotoluene, and the corresponding second crystallisation points.

Added *m*-nitrotoluene per cent.	Second crystallisation point.	Added *m*-nitrotoluene per cent.	Second crystallisation point.
0·5	– 14·9°	2·6	– 16·1°
1·1	– 15·3	3·4	– 16·5
1·7	– 15·65	4·3	– 17·0
2·2	– 15·9	5·1	– 17·4
		9·05	– 19·3

Examination of Mononitrotoluene.—Samples of mononitrotoluene were prepared under varying conditions of nitration as detailed in Table V, and the resulting products analysed by method I. The effect of conditions on the composition is not large, although low temperature reduces the proportion of *m*-nitrotoluene and increases the proportion of *p*-nitrotoluene. When a small bulk of mixed acid is used, the nitration appears to proceed too vigorously for the temperature effect to be obtained.

TABLE V.

Toluene.	Weight of nitrating acid.			Temp.	Crystallisation points.		Calculated composition.		
	H_2SO_4.	HNO_3.	H_2O.		Initial.	Second.	Ortho.	Meta.	Para.
75		282	18	40°	30·8°	– 17·35°	60·7	4·3	35
,,		282	18	0	31·7	– 18·4	60·3	2·5	37·2
35	58·7	23·8	17·5	50	30·3	– 17·3	62·2	4·3	33·5
,,	,,	,,	,,	40	29·8	– 17·2	63·6	4·2	32·2
,,	,,	,,	,,	20	30·35	– 17·4	61·9	4·5	33·6
,,	,,	,,	,,	0	30·6	– 17·45	61·1	4·5	34·4
,,	112	,,	38·2	40	30·25	– 17·1	62·7	3·9	33·4
36	,,	,,	,,	0	31·3	– 16·8	60·5	3.3	36·2

Mononitrotoluene prepared under the conditions recorded for the fifth sample in Table V was examined by method II (both variants).

(*a*) The second setting point, $-17·4°$, corresponds with 5·1 on the curve *B M* (Table IV).

After the addition of 2 per cent. of *m*-nitrotoluene, the second setting point, $-18·5°$, corresponds with 7·4 on curve *B M*.

Here $p = 70$, $d = 5·1$, $g = 7·4$, and $h = 2$.

Hence $z = \dfrac{5·1 \times 2}{2·3} = 4·4$, and $x = \dfrac{70 \times 2}{2·3} = 61$.

Therefore the composition is *o*- 61, *m*- 4·4, and *p*- 34·6.

(*b*) The second setting point, $-17·4°$, corresponds with 5·1 on curve *B M* (Table IV).

After the addition of an equal part of mixture *B* (70 per cent. of *o*- and 30 per cent. of *p*-) the second setting point, $-16°$, corresponds with 2·4 on curve *B M*.

Here $p = 70$, $d = 5·1$, $g = 2·4$, and $k = 70$.

Hence $x = \dfrac{kg}{d - g} = \dfrac{70 \times 2·4}{2·7} = 62·2$

and $z = \dfrac{d\,k\,g}{p(d - g)} = \dfrac{5·1 \times 70 \times 2·4}{70 \times 2·7} = 4·5$.

Therefore the composition is *o*- 62·2, *m*- 4·5, and *p*- 33·3.

Remarks.—Mononitrotoluene prepared under the usual conditions of nitration will contain approximately

o-nitrotoluene	62 per cent. $\pm$ 1.
p-nitrotoluene	33·5 to 32 per cent.
m-nitrotoluene	4·5 to 4·2 per cent.

These proportions do not appear to be affected sufficiently by variations in the process to make the suppression of *m*-nitrotoluene feasible, and therefore the influence of all three isomerides must be considered in the subsequent stages of nitration.

Dinitration.

Previous Work.—There appears to be in the literature no account of quantitative work on the dinitration of *o*-nitrotoluene. It is usually stated, without reference, that *p*-nitrotoluene gives 2 : 4-dinitrotoluene only. Sirks (*Rec. trav. chim.*, 1907, **27**, 208) found that *m*-nitrotoluene gave more than 50 per cent. of 3 : 4-dinitrotoluene, and more 2 : 3- than 2 : 5-dinitrotoluene.

Reference Curves.—As *o*-nitrotoluene gives on nitration 2 : 4,

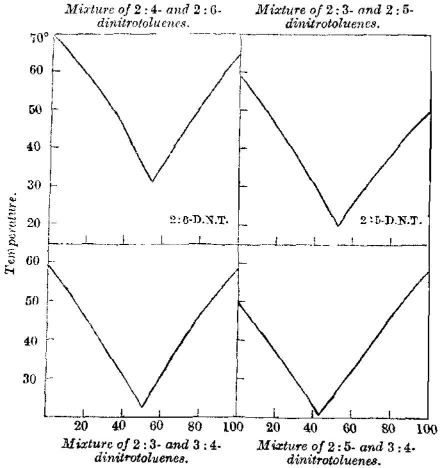
and 2 : 6-dinitrotoluenes, the binary fusion curve for these two isomerides is important.

Giua (*Ber.*, 1914, **47**, 1721) gives results which do not agree well with ours, given below in Table VI and Fig. 3.

TABLE VI.

2 : 6-Dinitro-toluene per cent.	Crystallisation point.	2 : 6-Dinitro-toluene per cent.	Crystallisation point.
0	69·8°	61·8	37·15°
9·83	64·5	65·2	39·95
27·89	53·95	70·9	44·55
33·43	49·95	73·6	46·25
39·5	45·0	77·5	49·0
44·63	39·75	81·7	52·25
48·14	35·95	83·9	53·95
50·0	34·75	90·8	59·05
51·95	33·15	95·2	61·45
55·75	32·05	100	64·65

FIG. 3.



Percentage of 3 : 4-*dinitrotoluene.*

The nitration of *m*-nitrotoluene gives 3 : 4-, 2 : 3-, and 2 : 5-dinitrotoluenes. The binary fusion curves for these substances

(Fig. 3) were drawn from the data in Tables VII, VIII, and IX and used in the examination of the nitration of *m*-nitrotoluene.

TABLE VII.

2 : 3- and 3 : 4-Dinitrotoluenes.

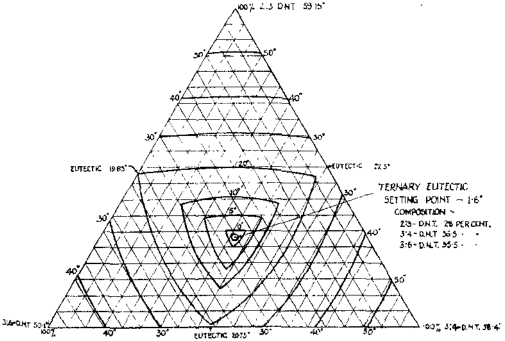
3 : 4-Dinitro-toluene per cent.	Crystal-lisation point.	Eutectic.
20	45·75°	
40	30·05	
45	26·9	22·5
50·5	22·5	22·5
55	26·5	22·5
60	29·5	
80	46·5	

TABLE VIII.

3 : 4- and 2 : 5-Dinitrotoluenes.

2 : 5-Dinitro-toluene per cent.	Crystal-lisation point.	Eutectic.
0	58·4°	
20	45·95	
40	31·9	
60	22·85	20·75
80	37·15	
100	50·1	

FIG. 4.



Ternary setting-point diagram. Mixtures of 2 : 3-, 3 : 4-, *and* 3 : 6-*dinitrotoluenes.*

TABLE IX.

2 : 3- and 2 : 5-Dinitrotoluenes.

2 : 5-Dinitrotoluene per cent.	Crystallisation point.	Eutectic.
0	59·15°	
20	45·85	
40	30·4	19·65
60	26·1	19·85
80	38·45	
100	50·1	

The ternary diagram for these three isomerides was also prepared (Fig. 4)

Examination of Dinitrotoluene.—The nitration of each of the isomeric mononitrotoluenes, and of the mononitration product of toluene obtained under the conditions described in Table V, to dinitrotoluene was carried out as follows :—

Fifty grams of mononitrotoluene were nitrated with 240 grams of a mixed acid of composition : sulphuric acid 77, nitric acid 11·3, and water 11·7 per cent.

The mononitrotoluene was added at 40—45°, and the temperature was finally raised to 70° and maintained for thirty minutes. The acid was then diluted with 40 c.c. of water, and the product separated, washed, and dried. The yield was about 91 per cent. The results obtained were as follows : *p*-nitrotoluene gave 2 : 4-dinitrotoluene only, crystallisation point 69·7°; *o*-nitrotoluene gave a mixture of 2 : 4- and 2 : 6-dinitrotoluenes, crystallisation point 50° (reference to the curve in Fig. 3 gives 66·6 parts of 2 : 4- and 33·3 parts of 2 : 6-dinitrotoluene from *o*-nitrotoluene); and *m*-nitrotoluene gave a mixture of 3 : 4-, 2 : 3-, and 2 : 5-dinitrotoluenes of crystallisation point 22·8°. The last mixture was not extensively studied, but the single sample prepared corresponded in crystallisation point with a mixture of 55, 25, and 20 per cent. of 3 : 4-, 2 : 3-, and 2 : 5-dinitrotoluenes respectively.

The crude mononitrotoluenes on nitration gave a crystallisation point varying from 55·6° to 56·7°.

A moderate-scale nitration of mononitrotoluene manufactured at a Government factory gave a dinitrotoluene of crystallisation point 56°. This, on the curve in Fig. 3, corresponds with 74·8 per cent. of 2 : 4-dinitrotoluene. The composition of commercial dinitrotoluene may therefore be taken as 2 : 4-dinitrotoluene 74·8 per cent., 2 : 6-dinitrotoluene 20·7 per cent., 3 : 4-dinitrotoluene 2·5 per cent., 2 : 3-dinitrotoluene 1·1 per cent., and 2 : 5-dinitrotoluene 0·9 per cent.

Trinitration.

Examination of Trinitrotoluene.—The nitration of each of the isomeric mononitrotoluenes was carried as out follows : 100 grams of mononitrotoluene were nitrated with 1000 grams of acid of the composition : sulphuric acid 78, nitric acid 17·5, and water 4·5 per cent.

The nitrations were carried out with gradual rise of temperature from 50° to 120° during five hours. The nitration product was precipitated with an excess of water, washed, and dried. *o*-Nitrotoluene gave 156 grams of 2 : 4 : 6-trinitrotoluene of crystallisation point 79·8°, *p*-nitrotoluene gave 158 grams, of crystallisation point 80·2°,

and *m*-nitrotoluene gave 144 grams of a mixture of trinitrotoluenes, of crystallisation point 73·8°.

Analysis of Crude Trinitrotoluene.—From the results obtained above, it is clear that crude trinitrotoluene may be regarded as composed of three essential components :

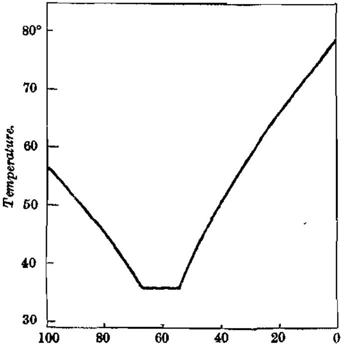
(1) Pure 2 : 4 : 6-trinitrotoluene.

(2) The mixture of trinitrotoluenes derived from *m*-nitrotoluene, and

(3) Crude dinitrotolueue, of crystallisation point close to 56°, the presence of which is due to incomplete nitration under manufacturing conditions.

Fig. 5.

Change of crystallisation point in course of nitration of dinitrotoluene.



The binary fusion curves for these three materials and the ternary fusion diagram were therefore mapped and from the ternary diagram all the desired information about any particular sample of crude trinitrotolueue could be obtained after its crystallisation point had been determined.

Information derived from the Ternary Diagram for Crude Trinitrotoluene.—The course of nitration as shown by the change in crystallisation point and the degree of completeness of nitration reached at any stage of the trinitration are given by Fig. 5, taken from the ternary diagram. If the crystallisation point or setting point is taken wet, the temperature is 5° lower.

Table X gives the composition of crude trinitrotoluene corresponding with varying crystallisation points.

TABLE X.

Crystallisation point.	Percentage composition. 2 : 4 : 6-Trinitrotoluene.	Other isomerides.	Dinitrotoluene.
78°	95·2	4·0	0·8
77	93·7	3·9	2·4
76	92·4	3·8	3·8
75	90·8	3·8	5·4
74	89·2	3·7	7·1

Table XI gives the composition at various temperatures of the liquid phase in crude trinitrotoluene of crystallisation point 76°. This is obtained by following the course of crystallisation of mixtures of this composition on the ternary diagram, the production of the line joining the points representing 2 : 4 : 6-trinitrotoluene and the composition in question, and reading off the composition at the isothermal lines.

TABLE XI.

	2 : 4 : 6-Trinitrotoluene.	Other isomerides.	Dinitrotoluenes.
Original composition	92·4	3·8	3·8
Composition of liquid phase at 60°	67·6	16·2	16·2
,, ,, ,, ,, ,, 50°	57·6	21·2	21·2
,, ,, ,, ,, ,, 40°	50·8	24·6	24·6
,, ,, ,, ,, ,, 30°	45·0	27·5	27·5

The percentage of oil in crude trinitrotoluene of setting point 76° at various temperatures can be calculated from Table XI. Table XII gives the results obtained.

TABLE XII.

Temp.	Oil content.
60°	23·4
50	17·9
40	15·5
30	13·8

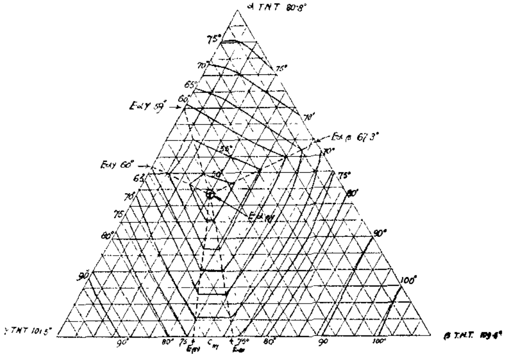
The loss on purification by such processes as centrifuging, washing with cold alcohol, or the sulphite process depends on the composition of the crude trinitrotoluene.

The last process removes only the isomeric trinitrotoluenes, raising the crystallisation point by 2·4°; the crystallisation point of the original crude material must therefore be high for this process to give purified material of a crystallisation point of 80°.

Further Investigation of the Trinitrotoluenes formed by Nitration.

Previous Work.—Molinari and Giua (*Rendiconti del Reale Institute de Scienza e Lettere*, 1913, **46**, fasc. II) investigated the by-products of trinitrotoluene manufacture and obtained by distillation in a vacuum a product melting at 79·5° which they considered to be 2 : 3 : 5- or 2 : 3 : 6-trinitrotoluene. Will (*Ber.*, 1914, **47**, 704) states positively that as the result of exhaustive investigation and extensive modification of the conditions of nitration, nothing but

FIG. 6.



Ternary fusion diagram for α-, β-, and γ-trinitrotoluenes.

Eαβ = *eutectic of α- and β-trinitrotoluenes.*
Eβγ = *eutectic of β- and γ-trinitrotoluenes* 73·5°.
Eαγ = *eutectic of α- and γ-trinitrotoluenes.*
Eαβγ = *ternary eutectic* 44·4°. *Composition* α 43·5 %, β 20·0 %, γ 36·5 %.
Cβγ = *compound* βγ. *Setting point* 74·5°.

the three well-known isomeric trinitrotoluenes are formed by the nitration of toluene, that is, 2 : 4 : 6-, 2 : 3 : 4-, and 3 : 4 : 6-trinitrotoluenes.

Reference Curves.—As a first step, the binary fusion curves for the three isomeric trinitrotoluenes, 2 : 4 : 6-, 2 : 3 : 4-, and 3 : 4 : 6-, were mapped and the ternary fusion diagram for the three isomerides was produced.

The results are shown in Table XIII and Fig. 6.

TABLE XIII.

Trinitrotoluene.			
2 : 4 : 6- (α-).	2 : 3 : 4- (β-).	3 : 4 : 6- (γ-).	Crystallisation point.
100			80·8°
80	20		74·2
59	41		67·3 eutectic.
40	60		82·6
20	80		96·8
	100		109·5
80		20	69
70		30	59 eutectic.
60		40	59·5
52		48	60 eutectic.
40		60	72·8
20		80	94·2
		100	101·5
	80	20	96·2
	60	40	82·7
	47·5	52·5	73·5 eutectic.
	40	60	74·3
	37	63	73·5 eutectic.
	20	80	78·5

The ternary fusion diagram was completed from data furnished by mixtures of all three isomerides. The ternary eutectic was found to have a crystallisation point of 44·4° and the composition 43·5 per cent. of 2 : 4 : 6-, 20 per cent. of 2 : 3 : 4-, and 36·5 per cent. of 3 : 4 : 6-trinitrotoluene.

The product of trinitration of *m*-nitrotoluene had a crystallisation point of 73·8°, and on addition to 2 : 4 : 6-trinitrotoluene gave a fusion curve with a minimum at 38·4° corresponding with the composition 44·5 per cent. of 2 : 4 : 6-trinitrotoluene. As this minimum was 6° lower than the ternary eutectic for 2 : 4 : 6- 2 : 3 : 4-, and 3 : 4 : 6-trinitrotoluenes, it was taken as an indication of the presence of another isomeride in the product of nitration of *m*-nitrotoluene.

Before further quantitative work could be done, it was necessary to investigate the preparation and properties of the rarer dinitrotoluenes and the trinitrotoluenes derivable from them. This work was undertaken by Brady, Drew, and others (T., 1920, **117**, 876, 1137). Ultimately Drew succeeded in isolating 2 : 3 : 6-trinitrotoluene as a product of the nitration of 2 : 3-dinitrotoluene and 2 : 5-dinitrotoluene.

A comparison of the thermal analysis of the products of nitration with the fusion curves of 2 : 3 : 4- and 2 : 3 : 6-trinitrotoluenes and 2 : 3 : 6- and 3 : 4 : 6-trinitrotoluenes indicated that 2 : 3-dinitrotoluene gave 16 per cent. of 2 : 3 : 6-trinitrotoluene, and 2 : 5-dinitrotoluene 13 per cent. Brady (private communication) has

found that the nitration of 3 : 4-dinitrotoluene yields 83 parts of 3 : 4 : 6- and 17 parts of 2 : 3 : 4-trinitrotoluene in the product.

From the above results the proportions of the isomeric trinitrotoluenes obtained on nitration of *m*-nitrotoluene are derivable from the composition of the product of dinitration of *m*-nitrotoluene.

	Trinitrotoluene.		
	3 : 4 : 6-	2 : 3 : 4-	2 : 3 : 6-
Thus 55 parts of 3 : 4-dinitrotoluene give	45·7	9·3	
,, 25 ,, ,, 2 : 3- ,, ,,		21	4
,, 20 ,, ,, 2 : 5- ,, ,,	17·4		2·6
Hence *m*-nitrotoluene gives	63·1	30·3	6·6

The crystallisation point of a mixture of this composition agrees well with that of the direct nitration product of *m*-nitrotoluene, 73·8°.

Under usual conditions of nitration, the nitro-derivatives obtained at each stage from toluene may therefore be summarised as follows :

Mononitrotoluenes.		Dinitrotoluenes.		Trinitrotoluenes.	
ortho-	62 per cent.	2 : 4-	74·8 per cent.	2 : 4 : 6-	95·5 per cent.
para-	33·5 ,, ,,	2 : 6-	20·7 ,, ,,	3 : 4 : 6-	2·9 ,, ,,
meta-	4·5 ,, ,,	3 : 4-	2·5 ,, ,,	2 : 3 : 4-	1·3 ,, ,,
		2 : 3-	1·1 ,, ,,	2 : 3 : 6-	0·3 ,, ,,
		2 : 5-	0·9 ,, ,,		

Our thanks are due to the Director of Artillery, War Office, for permission to publish this account.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, January 17th*, 1922.]

XXXV.—*Isomeric Citraconyl Hydrazides.*

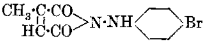
By FREDERICK DANIEL CHATTAWAY and DERIC WILLIAM PARKES.

THE citraconyl hydrazides have been little studied though various members of the series have been prepared by Michael (*Amer. Chem. J.*, 1887, **9**, 180), Fichter and Füeg (*J. pr. Chem.*, 1906, [ii], **74**, 297), Chattaway and Hodgson (T., 1916, **106**, 586), and Chattaway and Ellington (T., 1916, **109**, 590).

The existence of two series of phthalyl hydrazides made it appear probable that isomeric citraconyl hydrazides, containing a five- and a six-atom ring respectively, would be produced by the inter-

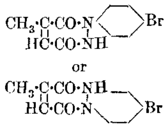
This has now been established and two series of citraconyl hydrazides have been obtained, which, as in the case of the phthalyl hydrazides, may be termed the α- and the β-series, the former designation being used for the yellow, the latter for the colourless, isomerides, for example:

α-Citraconyl-*p*-bromophenylhydrazide (yellow).



(I.)

β-Citraconyl-*p*-bromophenylhydrazide (colourless).

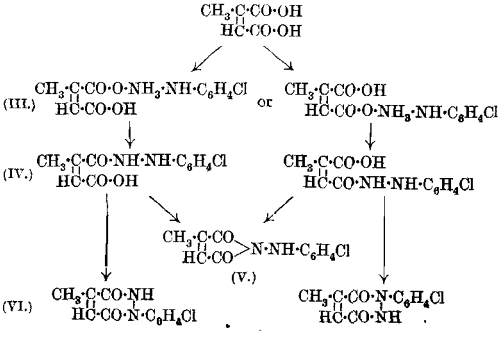


(II.)

When an ethereal solution of citraconic acid is allowed to act on an aromatic hydrazine, a colourless salt is first produced. This, however, passes readily into the hydrazide of citraconic acid and this into one of possible citraconyl hydrazides, water being eliminated at each stage.

Two configurations are possible for the salts, for the citraconic acid hydrazides, and for the β-citraconyl hydrazides: which is to be assigned to the compounds actually obtained cannot at present be decided; they, however, appear to be chemical individuals and not mixtures of the two possible isomerides.

In the case of *p*-chlorophenylhydrazine, the reactions may be represented thus:



If citraconic anhydride is used instead of the acid, the hydrazide of citraconic acid is at once formed and yields the citraconyl hydrazides as above.

The β-citraconyl hydrazides all dissolve in dilute alkali and are reprecipitated unchanged on acidifying. They all reduce a warm ammoniacal solution of silver nitrate containing sodium hydroxide.

Experimental.

p-*Chlorophenylhydrazine Citraconate* (Formula III).—When a cooled ethereal solution of citraconic acid (1 mol.) is added to a similarly cooled solution of *p*-chlorophenylhydrazine (1 mol.), a pale yellow liquid is produced, from which p-*chlorophenylhydrazine citraconate* separates as a crystalline, almost colourless solid. It can be recrystallised from warm ether and from warm alcohol, in both of which it is moderately easily soluble, although heating must be avoided, as it very easily loses water.

It separates from ether or alcohol in almost colourless, compact prisms which, when rapidly heated, melt at 119° with loss of water (Found: Cl = 12·96. $C_{11}H_{13}O_4N_2Cl$ requires Cl = 13·01 per cent.).

The salt dissolves in water, yielding a pale yellow solution with an acid reaction to litmus. It is instantly decomposed by aqueous caustic alkali, *p*-chlorophenylhydrazine being liberated. On boiling its aqueous solution, the salt loses water, citraconic acid *p*-chlorophenylhydrazide separating in yellow, oily drops.

Citraconic Acid p-*Chlorophenylhydrazide* (Formula IV).—This compound may be prepared by heating an aqueous solution of *p*-chlorophenylhydrazine citraconate, but is best made hy mixing ethereal solutions of equivalent quantities of citraconic anhydride and *p*-chlorophenylhydrazine. A vigorous reaction takes place with the evolution of considerable heat. On cooling, an orange-yellow solid separates, consisting of a mixture of citraconic acid *p*-chlorophenylhydrazide with a small quantity of the α- and β-citraconyl hydrazides.

On treating the mixture with cold alcohol the citraconic acid hydrazide and the α-citraconyl hydrazide in great measure dissolve whilst the bulk of the small quantity of the β-citraconyl hydrazide formed remains as a sparingly soluble residue.

To prepare the *citraconic acid* p-*chlorophenylhydrazide*, such an alcoholic solution is diluted with water, the solid which separates dissolved in dilute alkali, and the citraconic acid hydrazide precipitated by cautious addition of hydrochloric acid.

It is easily soluble in chloroform, but sparingly soluble in light petroleum, and is best obtained crystalline by dissolving in chloro-

form and adding warm light petroleum. It then separates in orange-coloured, crystalline nodules.

It melts when rapidly heated at 142—143° with loss of water and formation of a mixture of the α- and β-citraconyl-*p*-chlorophenylhydrazides (Found: Cl = 13·59. $C_{11}H_{11}O_3N_2Cl$ requires Cl = 13·93 per cent.).

*α-Citraconyl-*p*-chlorophenylhydrazide* (Formula V).—When citraconic acid *p*-chlorophenylhydrazide is heated with alcohol, it slowly loses water and becomes converted into a mixture of the α- and β-citraconyl-*p*-chlorophenylhydrazides. The dehydration is best effected by heating the acid for a short time at a few degrees above its melting point until water vapour ceases to be disengaged. A resin-like mass is left on cooling; from this, after powdering, α-citraconyl-*p*-chlorophenylhydrazide, which is produced in by far the larger amount, can be extracted by alcohol.

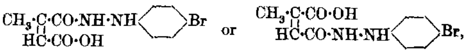
*α-Citraconyl-*p*-chlorophenylhydrazide* separates from hot alcohol, in which it is easily soluble, in compact, bright yellow, rhombic octahedra which melt at 140·5° (Found: Cl = 14·89. $C_{11}H_9O_2N_2Cl$ requires Cl = 14·99 per cent.).

*β-Citraconyl-*p*-chlorophenylhydrazide* (Formula VI).—This compound, which is formed in comparatively small amount when citraconic acid *p*-chlorophenylhydrazide is heated, may easily be obtained from the residue left after extracting the α-isomeride with alcohol. It is best to recrystallise it several times from glacial acetic acid, then to dissolve it in dilute alkali, in which it dissolves fairly easily and from which it is reprecipitated unchanged on addition of hydrochloric acid, and finally again to recrystallise it from glacial acetic acid.

It dissolves moderately easily in boiling glacial acetic acid, and separates in colourless leaflets which begin to melt with decomposition at about 295°. Like all the other β-citraconyl hydrazides, it reduces a warm ammoniacal solution of silver nitrate containing caustic alkali (Found: Cl = 14·99. $C_{11}H_9O_2N_2Cl$ requires Cl = 14·99 per cent.).

The *p*-bromo-compounds may all be prepared in a similar way to the corresponding chloro-derivatives.

*Citraconic acid *p*-bromophenylhydrazide*,



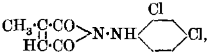
crystallises from a mixture of chloroform and light petroleum in orange-yellow nodules. It melts at 130° with loss of water (Found: Br = 26·18. $C_{11}H_{11}O_3N_2Br$ requires Br = 26·72 per cent.).

α-Citraconyl-p-*bromophenylhydrazide* (Formula I) crystallises from alcohol, in which it is readily soluble, in brilliant yellow, rhombic octahedra melting at 129° (Found: Br = 28·47. $C_{11}H_9O_2N_2Br$ requires Br = 28·44 per cent.).

β-Citraconyl-p-*bromophenylhydrazide* (Formula II) crystallises from boiling glacial acetic acid, in which it is moderately readily soluble, in thin, colourless plates, which melt with decomposition at 290° (Found: Br = 28·56. $C_{11}H_9O_2N_2Br$ requires Br = 28·44 per cent.).

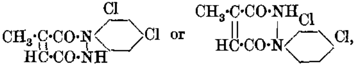
The reaction between citraconic anhydride and 2 : 4-dichlorophenylhydrazine follows a similar course, but the elimination of water takes place more readily and the β-isomeride is produced in relatively smaller amount.

α-Citraconyl-2 : 4-*dichlorophenylhydrazide*,



crystallises from hot alcohol, in which it is readily soluble, in bright yellow prisms which melt at 126° (Found: Cl = 26·03. $C_{11}H_8O_2N_2Cl_2$ requires Cl = 26·17 per cent.).

β-Citraconyl-2 : 4-*dichlorophenylhydrazide*,



crystallises from hot glacial acetic acid in small, colourless crystals which do not melt below 320°, but at a higher temperature blacken and decompose (Found: Cl = 26·15. $C_{11}H_8O_2N_2Cl_2$ requires Cl = 26·17 per cent.).

α-Citraconyl-2 : 4-dibromophenylhydrazide crystallises from hot alcohol, in which it is moderately easily soluble, in pale yellow, hair-like needles which melt at 145—146° (Found: Br = 44·21. $C_{11}H_8O_2N_2Br_2$ requires Br = 44·41 per cent.).

The β-compound, if produced, is formed in such small amount that up to the present it has not been isolated.

Citraconic acid o-*tolylhydrazide* crystallises from hot acetone, in which it is readily soluble, in compact, yellow, rhombic plates which melt at 132° with effervescence and liberation of water vapour. It is very easily soluble in ether, alcohol, or glacial acetic acid, and sparingly soluble in benzene, carbon disulphide, or light petroleum (Found: C = 61·71; H = 6·21; N = 11·81. $C_{12}H_{14}O_3N_2$ requires C = 61·50; H = 6·03; N = 11·97 per cent.).

To prepare the α- and β-citraconyl-*o*-tolylhydrazides, citraconic

acid *o*-tolylhydrazide is best heated at 135° until water vapour is no longer given off. On dissolving the melt in a small quantity of boiling alcohol, the α-isomeride first separates on cooling; on allowing the mother-liquor to stand, the β-isomeride, which is formed in relatively much smaller amount, is slowly deposited.

α-Citraconyl-o-*tolylhydrazide* separates from boiling alcohol, in which it is very soluble, in small, thin, yellow plates which melt at 135° (Found: N = 12·93. $C_{12}H_{12}O_2N_2$ requires N = 12·96 per cent.).

β-Citraconyl-o-*tolylhydrazide* crystallises from boiling alcohol, in which it is only sparingly soluble, in stout, colourless prisms which melt at 252—253° (Found: N = 13·01. $C_{12}H_{12}O_2N_2$ requires N = 12·96 per cent.).

β-Citraconyl-p-*tolylhydrazide*.—The corresponding α-citraconyl-*p*-tolylhydrazide, m. p. 169°, was prepared by Fichter and Füeg (*loc. cit.*) from *p*-tolylhydrazine and an aqueous solution of citraconic acid. The β-isomeride is most easily obtained by mixing somewhat dilute ethereal solutions of equivalent quantities of *p*-tolylhydrazine and citraconic anhydride. The mixture becomes warm and on standing for some days at the ordinary temperature *β-citraconyl*-p-*tolylhydrazide* separates. It crystallises from hot alcohol, in which it is sparingly soluble, in brilliant, colourless prisms which melt at 259° (Found: C = 66·67; H = 5·67; N = 12·89. $C_{12}H_{12}O_2N_2$ requires C = 66·63; H = 5·60; N = 12·96 per cent.).

If the dilute ethereal mother-liquor after removal of the β-isomeride is allowed spontaneously to evaporate, citraconic acid *p*-tolylhydrazide separates in yellow nodules. These on heating give off water and yield the α-citraconyl-*p*-tolylhydrazide, m. p. 169°, described by Fichter and Füeg, together with a further quantity of the β-isomeride.

All the α-citraconyl hydrazides give a peculiar colour reaction. When to any one of these compounds dissolved in alcohol a few drops of aqueous caustic alkali are added, a deep crimson colour is produced. Gentle warming causes this colour to become much fainter and almost to disappear. It similarly almost disappears on standing or on adding excess of alkali. The citraconic acid hydrazides do not give the reaction, whilst such of the citraconanils as have been examined do.

It may be recalled that isatin under like conditions gives a similar reaction.

This investigation is part of the work carried out by one of us (D. W. P.), while holding a Salters' Fellowship.

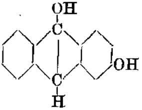
THE QUEEN'S COLLEGE,
OXFORD.

[*Received, January 10th*, 1922.]

XXXVI.—*Some Products of the Reduction of 2-Hydroxyanthraquinone.*

By Arthur George Perkin and Thomas William Whattam.

According to Liebermann and Simon (*Annalen*, 1882, **212**, 28) β-hydroxyanthranol (3-hydroxyanthranol)



is obtained when 2-hydroxyanthraquinone dissolved in ammonia is digested on the steam-bath with zinc dust, avoiding access of air, until an almost colourless liquid which does not quickly redden on exposure to air is produced. From the decanted liquid, by neutralisation, 3-hydroxyanthranol separates. Employing this process, however, with the apparatus described below, the yield of 3-hydroxyanthranol was found to vary considerably, and the cause of this defect was accordingly studied. As a result, it was found that the longer the digestion the smaller is the amount of the anthranol obtained, and that other compounds insoluble in the ammoniacal liquid are gradually produced. After numerous experiments, the following method for the separation of these by-products was found to give the best results.

Experimental.

A solution of 100 grams of crude 2-hydroxyanthraquinone (from commercial 2-aminoanthraquinone *) in 800 grams of ammonia (*d* 0·880) and 500 c.c. of water, contained in an Erlenmeyer flask fitted with a cork provided with a short glass tube constricted at one end so as to avoid free access of air, was heated on the water-

* For the preparation of 2-hydroxyanthraquinone in this manner, 55·6 grams of 2-aminoanthraquinone dissolved in 556 grams of sulphuric acid are treated at 0° with 21 grams of sodium nitrite during a quarter of an hour, with vigorous stirring. The mixture is now stirred at the ordinary temperature for three and a half hours and then poured on to ice, and the product is raised to the boiling point and boiled for half an hour. The precipitated 2-hydroxyanthraquinone thus obtained averages 99·5 per cent. of the theoretical amount.

bath. Two hundred grams of well reactive zinc dust were added a little at a time and the mixture was heated for two hours, 50 c.c. of dilute ammonia being added every quarter of an hour. On digestion for two hours longer, the zinc residue caked together and became interspersed with yellow, crystalline matter. The liquid was now decanted into dilute hydrochloric acid, giving a grey precipitate (*A*), and the zinc residue was washed with water, ground into a paste, and treated with 15 per cent. hydrochloric acid, first in the cold over-night and subsequently on the steam-bath until nothing more dissolved. The brown residue was collected, dried on tile, extracted repeatedly with absolute alcohol, and the extract concentrated to about 120 c.c. Addition of benzene, a little at a time, caused the gradual separation of crystals, which increased on long keeping. These were collected, washed with a mixture of benzene and alcohol, and dried (*B*).

The alcohol-benzene mother-liquor, on concentration to one-half its volume, gave a further deposit (*C*), consisting of a substance distinct from (*B*). From the final filtrate, by evaporation, much tarry residue was obtained, from which, by treatment with acetone, a further amount of (*C*) separated. Finally, from the acetone washings some 3-hydroxyanthranol could be isolated.

For purification, (*B*) was stirred with a small amount of acetone and filtered to remove a trace of the compound (*C*), which is very sparingly soluble in this solvent. The clear liquid was treated at the boiling point with benzene, and the crystals deposited were again treated in a similar manner. The product was finally crystallised from a minimum of pure acetone and washed with a mixture of benzene and alcohol (Found: C = 86·69; H = 5·13. $C_{28}H_{18}O_2$ requires C = 87·04; H = 4·66 per cent.).

This substance consisted of colourless, prismatic needles which, when heated, became brown at about 270° and melted at 278—281°. When exposed to light, it rapidly develops a reddish-brown tint, and on this account it is preferable during the purification to proceed as rapidly as possible and to avoid unnecessary exposure of its solutions, for should this brown impurity be allowed to form, it is difficult to remove without a considerable loss of material. The substance $C_{28}H_{18}O_2$ is soluble in dilute alkalis with a pale yellow colour, which, on exposure to air, very slowly becomes redder, whereas its solution in sulphuric acid is orange-brown and yields a yellowish-green precipitate on dilution.

On boiling with acetic anhydride and a trace of pyridine, a clear solution is quickly obtained, but as the digestion proceeds prismatic needles of the acetyl compound separate. They are purified by recrystallisation from a large volume of acetic anhydride [Found:

$C = 81 \cdot 67$; $H = 5 \cdot 04$. $C_{28}H_{16}O_2(C_2H_3O)_2$ requires $C = 81 \cdot 70$; $H = 4 \cdot 68$ per cent.].

This *diacetyl* derivative consists of long, prismatic needles which melt at about 303—304°, are sparingly soluble in acetic anhydride to form a blue fluorescent solution, and dissolve in sulphuric acid with an orange-brown coloration. Owing to its insoluble nature, it is difficult to hydrolyse in the usual way, even with fuming hydrochloric acid in the presence of acetic acid, and the acetyl derivative is therefore not useful for the purification of the original compound. The estimation of the acetyl groups was carried out by the acetic ester method, long digestion being necessary [Found: acetic acid = 25·47. $C_{28}H_{16}O_2(C_2H_3O)_2$ requires acetic acid = 25.53 per cent.].

The *dibenzoyl* derivative was prepared by employing five parts of benzoic anhydride and heating at 180° for one and a half hours. On pouring the melt into alcohol, a colourless precipitate separated, which was recrystallised from a mixture of benzene and alcohol. It consisted of needles which melted at 162—163°, and the solutions in benzene and alcohol possessed a blue fluorescence [Found: $C = 84 \cdot 47$; $H = 4 \cdot 74$. $C_{28}H_{16}O_2(CO \cdot C_6H_5)_2$ requires $C = 84 \cdot 84$; $H = 4 \cdot 55$ per cent.].

When a solution of the substance $C_{28}H_{18}O_2$ (p. 290) dissolved in methyl alcohol is treated with methyl-alcoholic potash and methyl sulphate, methylation readily occurs and the methyl ether separates from the liquid as the reaction proceeds. It is purified by crystallisation either from acetone or from a mixture of benzene and alcohol [Found: $C = 86 \cdot 68$; $H = 5 \cdot 45$. $C_{28}H_{16}(O \cdot CH_3)_2$ requires $C = 86 \cdot 95$; $H = 5 \cdot 31$ per cent.].

This *dimethyl* derivative crystallised in small needles melting at 284°, which were difficult to obtain in a completely colourless condition. Its solutions in acetone and benzene possess a fine violet fluorescence. When digested with hydriodic acid, it is but little attacked, and even in the presence of acetic anhydride the methyl groups could not be estimated in the usual way. At first sight it thus appeared that these could not be present as methoxyl and were probably attached to *meso*-carbon atoms, but this can scarcely be the case, for the reasons given below, and the resistance to demethylation must be due to the almost complete insolubility of the compound in the hydriodic acid. A molecular-weight determination gave the following result: 0·437 in 11·121 grams of naphthalene depressed the freezing point by 0·722°. $M = 375 \cdot 6$. Theory for $C_{30}H_{24}O_2$ requires $M = 416$.

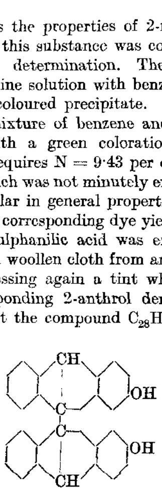
In order to determine, if possible, the position of the methyl groups, the methyl ether (1 gram) suspended in acetic acid was

treated at the boiling point with a solution of chromic acid (1 gram) in 2 c.c. of 50 per cent. acetic acid. Oxidation readily occurred, and after five minutes the addition of hot water caused the gradual separation of crystals. These, after recrystallisation from alcohol, consisted of pale yellow needles melting at 192—193° (Found: C = 75·77; H = 4·13. $C_{15}H_{10}O_3$ requires C = 75·63; H = 4·20 per cent.).

This compound has the properties of 2-methoxyanthraquinone, and its identity with this substance was confirmed by means of a mixed melting-point determination. The substance $C_{28}H_{18}O_2$ readily reacts in alkaline solution with benzenediazonium chloride, yielding a bordeaux-coloured precipitate. This was collected and crystallised from a mixture of benzene and alcohol; it dissolved in sulphuric acid with a green coloration [Found: N = 9·09. $C_{28}H_{16}O_2(N_2{\cdot}C_6H_5)_2$ requires N = 9·43 per cent.].

This derivative, which was not minutely examined, melts at about 250° and is very similar in general properties, although somewhat bluer in colour, to the corresponding dye yielded by 2-anthrol itself.

When diazotised sulphanilic acid was employed, the colouring matter obtained dyed woollen cloth from an acid bath a bordeaux-coloured shade, possessing again a tint which is bluer than that given by the corresponding 2-anthrol derivative. These results leave little doubt that the compound $C_{28}H_{18}O_2$ is 2 : 2′-*dihydroxydianthryl*,



2 : 2′-Dihydroxydianthryl resembles 2-anthrol in that, like the latter, it can be readily methylated by means of methyl alcohol in presence of sulphuric or hydrochloric acid. Thus addition of a little sulphuric acid to the gently boiling solution in methyl alcohol caused the gradual separation of a pale yellow, crystalline powder, and this, when the digestion had proceeded for half an hour, was collected, washed with dilute alcohol, and crystallised from acetone. The compound melted at 280° and proved to be identical with the dimethoxydianthryl described above.

Fraction C.—This product was purified by washing with cold acetone, in which it is very sparingly soluble (distinction from *B*), and subsequent crystallisation from alcohol (Found: C = 80·53,

80·28; H = 4·50, 4·65. $C_{28}H_{18}O_4$ requires C = 80·33; H = 4·33 per cent.).

In boiling acetone it dissolves to the extent of only 1 part in 500 parts, and separates on cooling mainly with acetone of crystallisation, which cannot be removed by heating at 100° (Found: C = 78·04, 77·72; H = 5·15, 4·99. $C_{28}H_{18}O_4,C_3H_6O$ requires C = 78·15; H = 5·04 per cent.).

Preparations crystallised in this manner, when digested with alkali and iodine, gave a distinct odour of iodoform, and a sample, on drying at 160°, lost 10·84 per cent. of acetone, the above formula requiring acetone = 12·18 per cent.

The substance $C_{28}H_{18}O_4$ is deposited from alcohol as small, colourless, prismatic needles, which melt somewhat indefinitely at about 300° and possess the characteristic property of becoming green shortly before fusion occurs. It is moderately soluble in boiling alcohol to give a non-fluorescent solution, and yields, with sodium hydroxide, a clear yellow liquid which, on exposure to air, slowly develops a red tint. Sulphuric acid dissolves it with a yellow coloration. It does not couple with benzenediazonium chloride in the ordinary manner. Heated with hydriodic acid (*d* 1·7) at the boiling point during half an hour, the compound $C_{28}H_{18}O_4$ yielded 3-hydroxyanthranol, which was recognised by means of its acetyl derivative melting at 154—155°.

According to the method employed, two distinct acetyl compounds can be prepared from the substance $C_{28}H_{18}O_4$. After it had been digested with boiling acetic anhydride for two hours, the addition of alcohol to the cooled solution caused the separation of pale yellow crystals. For purification, these were dissolved in a minimum of boiling acetic anhydride, and the solution was treated with animal charcoal, filtered, and alcohol added to the filtrate. Colourless, prismatic needles separated, which melted at 190—191° and were soluble in sulphuric acid with a yellow coloration [Found: C = 76·01; H = 4·52. $C_{28}H_{16}O_4(C_2H_3O)_2$ requires C = 76·49; H = 4·38 per cent.].

An acetyl determination by the acetic ester method gave acetic acid = 24·25, the theory for two acetyl groups requiring acetic acid = 23·9 per cent. The compound is readily soluble in benzene, yielding a blue, fluorescent liquid, and its solution in alcohol, in which it dissolves sparingly, is also fluorescent. In acetic acid, there is no fluorescence.

A molecular-weight determination of the acetyl compound gave the following result:

0·5520 in 10·18 of naphthalene gave $\Delta = 0·74°$. $M = 505·7$. Calc. for $C_{28}H_{16}O_4(C_2H_3O)_2$, $M = 502$.

On the other hand, if the acetylation is carried out by boiling with acetic anhydride for one hour in the presence of a trace of pyridine, the addition of alcohol causes the deposition of a different acetyl derivative. This, purified in the same manner as the diacetyl compound described above, formed colourless plates melting at 265°, which were soluble in sulphuric acid with a magenta coloration [Found: C = 73·73; H = 4·50. $C_{28}H_{14}O_4(C_2H_3O)_4$ requires C = 73·72; H = 4·44 per cent.].

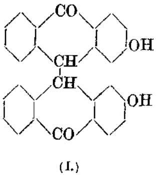
An acetyl determination by the acetic ester method gave acetic acid = 40·4, the above formula requiring acetic acid = 40·95 per cent. This *tetra-acetyl* derivative is readily soluble in benzene with formation of a blue, fluorescent solution. When it was hydrolysed with fuming hydrochloric acid in the presence of acetic acid in the usual manner, the original compound, $C_{28}H_{18}O_4$, separated as small needles, and these, when digested with boiling acetic anhydride, gave the diacetyl compound, $C_{28}H_{16}O_4Ac_2$, m. p. 190—191°.

Furthermore, this diacetyl compound, when digested with acetic anhydride and pyridine, was converted into the tetra-acetyl derivative soluble in sulphuric acid with a magenta coloration. As attempts to prepare the methyl ether of the compound $C_{10}H_{18}O_4$ by means of alkali and methyl sulphate were unpromising, diazomethane was employed.

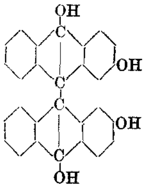
The substance (1 gram), suspended in 25 c.c. of pure acetone, was treated with an ethereal solution of diazomethane in some excess, and the mixture allowed to stand over-night. Crystals had then separated, and after evaporating the mixture to dryness, these were purified by crystallisation from acetone [Found: C = 80·77; H = 4·73; CH_3 = 6·88. $C_{28}H_{16}O_2(O{\cdot}CH_3)_2$ requires C = 80·72; H = 4·93; CH_3 = 6·73 per cent.].

This *dimethyl ether* forms colourless needles melting at 217°, is moderately soluble in acetone, and dissolves in sulphuric acid with a yellow coloration.

The compound $C_{28}H_{18}O_4$ is thus evidently 3 : 3′-*dihydroxydianthrone* (I),



(I.)



(II.)

By acetylation in the presence of pyridine, enolisation evidently occurs, the tetra-acetyl compound of the dianthranol (II) being produced.

Reduction of Dihydroxydianthrone.

This was carried out in a similar manner as the reduction of 2-hydroxyanthraquinone described above, employing 5 grams of the dianthrone, 25 c.c. of water, 45 c.c. of ammonia (*d* 0·880), and 10 grams of zinc dust. The digestion was carried out for four and a half hours, and during the first two hours 10 c.c. of dilute ammonia were added after each quarter of an hour. The supernatant liquid was poured into dilute hydrochloric acid, giving a colourless precipitate, and this was collected and dried. From this, by treatment with pure acetone, a trace of unattacked dihydroxydianthrone was recovered, whereas the soluble portion consisted of 3-hydroxyanthranol, which gave the acetyl derivative, m. p. 155°.

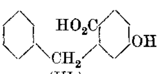
From the zinc residues, in the manner previously described, brown crystals of the dihydroxydianthryl were isolated, and these, after crystallisation from benzene and alcohol, gave the acetyl derivative melting at 302—303°.

Experiments were now carried out in the hope of reversing the procedure, that is, the oxidation of the 3-hydroxyanthranol to the dihydroxydianthrone. The former substance (1 gram), dissolved in 10 c.c. of boiling acetic acid, was treated with a solution of 0·9 gram of commercial ferric chloride in 1 c.c. of the same solvent. After digestion at the boiling point for a few minutes, yellowish-green crystals commenced to separate, and, when cold, these were collected and weighed 0·7 gram. These melted at about 300°, and by acetylation with acetic anhydride and pyridine gave an acetyl compound melting at 265°. This dissolved in sulphuric acid with a magenta-red coloration and was evidently the tetra-acetyl derivative of the dihydroxydianthranol referred to above. By treating the acetyl derivative of 3-hydroxyanthranol with ferric chloride, oxidation to dihydroxydianthrone takes place, hydrolysis of the acetyl groups also occurring during the reaction, and this process for the preparation of the dihydroxydianthrone is preferable owing to the readier oxidation of the more soluble, acetylated 3-hydroxyanthranol. Thus 1 gram of 3-acetoxyanthranol in 3 c.c. of acetic acid gave with 0·75 gram of ferric chloride a deposit of 0·5 gram of crystalline dihydroxydianthrone, and from the mother-liquor by cautious dilution with boiling water a further 0·2 gram of crystals was isolated. This corresponds with a yield of approximately 86 per cent. A specimen prepared by the latter method, after one crystal-

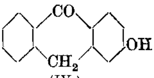
lisation from alcohol, gave C = 80·57; H = 4·25 (calc., C = 80·33; H = 4·33 per cent.).

This method of preparation of the dianthrone is obviously more advantageous than that described earlier, which involves the reduction of 2-hydroxyanthraquinone with zinc dust and ammonia.

The positions of the hydroxyl groups in this dihydroxydianthrone and in the 2 : 2′-dihydroxydianthryl described earlier in the paper follow from the known position of the hydroxyl group in 3-hydroxy-anthranol (or anthrone) (IV), from which both compounds may be considered to have been derived. Thus Bistrzychi and Yssel de Schepper (*Ber.*, 1898, **31**, 2794) obtained 3-hydroxyanthranol by treating the hydroxydiphenylmethanecarboxylic acid (III) with sulphuric acid.

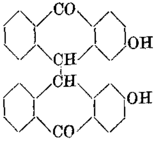


(III.)



(IV.)

Since 3 : 3′-dihydroxydianthrone is derived from the hydroxy-anthrone by oxidation, its formula must accordingly be represented as (V),



(V.)

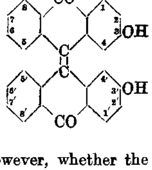
and again, since dihydroxydianthryl is obtained from the latter by reduction, the hydroxyls present in this substance must also occupy the same positions.

The investigation of the oxidation of other hydroxyanthranols or their acetyl derivatives with ferric chloride is in progress, and crystalline products have been obtained in this way from both deoxyalizarin and the anthranol of anthragallol, both of which apparently are dianthrone derivatives.

Oxidation of the Dihydroxydianthrone (Formula V).

With the object of obtaining the corresponding 2 : 2′-dihydroxy-dianthraquinone, experiments have been carried out on the action of permanganate on a suspension of the dianthrone in water, employ-

ng in the first case slightly more than the theoretical amount of this oxidising agent. After removal of manganese oxide with oxalic acid, there remained an orange, amorphous product soluble in sulphuric acid with a dull violet coloration. This evidently was a mixture and was extracted first with cold and subsequently with hot acetone, by which means a considerable quantity of a resinous impurity passed into solution. The residue was now dissolved in a large volume of boiling acetone, the solution evaporated, the bright orange-red crystals extracted repeatedly with boiling alcohol, and finally recrystallised from acetone. The substance thus obtained consisted of glistening, orange-red needles, which, when heated, appeared gradually to decompose above 300° and had not completely melted at 350°. Sulphuric acid dissolves it with a fine bluish-violet coloration, and dilute alkalis with a red tint similar to that given by 2-hydroxyanthraquinone itself. By acetylation with acetic anhydride and pyridine in the usual manner, an acetyl compound crystallising in golden-yellow needles is obtained, the solution of which in benzene is characterised by a strong green fluorescence. When heated, this compound undergoes incipient fusion between 160° and 170°, and as the temperature rises becomes again completely solid, and finally melts fairly sharply at 276°. The yield of this orange-red oxidation product has hitherto averaged not more than 10 per cent. of the dihydroxydianthrone employed, and further experiments will be carried out with the object of devising a more economical method for its preparation. The same compound has been obtained by one of us and G. G. Bradshaw in a somewhat unexpected manner from 2-hydroxyanthraquinone, and this fact has allowed of a more detailed examination of the compound, an account of which will be shortly laid before the Society. As a result, it seems highly probable that this substance has the formula $C_{28}H_{14}O_2(OH)_2$ and is 3 : 3′-dihydroxydianthraquinone;



it is still doubtful, however, whether the hydroxyl groups are in positions 3 and 3′ or 3 and 6′.

The Reduction of 2-Hydroxyanthraquinone with Aluminium Powder in the Presence of Dilute Alcohol and Ammonia.

Experiments on the reduction of 2-hydroxyanthraquinone with zinc dust and ammonia in the presence of dilute alcohol were carried out in the hope of discovering a more convenient method for the preparation of 2 : 2′-dihydroxydianthryl. These have been hitherto successful in so far that it has been ascertained that in this way 3-hydroxyanthranol is produced in good yield. By the employment of aluminium powder, however, an interesting result was obtained. Excess of aluminium powder was added to 10 grams of 2-hydroxyanthraquinone, 100 c.c. of 50 per cent. alcohol, and 90 c.c. of strong ammonia contained in a flask provided with a reflux condenser, and the mixture was gently heated on the water-bath. As the reaction, which at first was vigorous, proceeded, the liquid gradually became yellow and reddened on exposure to air. At this stage, which may occur after one hour's digestion, the ammonium salt of 3-hydroxyanthranol is mainly present. On continuing the digestion for a second hour, the ammoniacal solution no longer became red on exposure to air, and after filtration from the aluminium * residue, was neutralised with hydrochloric acid. The pale yellow flocks thus deposited were collected and, when dry, weighed 7 grams.

To identify this product, it was acetylated and the acetyl compound crystallised from benzene, from which it separated in colourless leaflets melting at 195° [Found: C = 81·62; H = 5·08; acetic acid = 24·6. $C_{14}H_9O(C_2H_3O)$ requires C = 81·36; H = 5·09; acetic acid = 25·4 per cent.].

The residual alcoholic liquid from the acetyl determination deposited, on cooling, colourless needles, which could be recrystallised from dilute alcohol and melted at 144·5—146°. These were insoluble in dilute alkali and evidently consisted of the ethyl ether of 2-anthrol.†

There can be no doubt, therefore, that this product of the reduction of 2-hydroxyanthraquinone with aluminium powder consists of 2-anthrol, as with this its reactions fully harmonise. The melting point of 2-anthryl acetate is given by Liebermann (*Annalen*, 1882, **212**, 26) as 198°, and that of 2-anthryl ethyl ether as 145—146° (Liebermann and Hagen, *Ber.*, 1882, **15**, 1427). According, again, to Liebermann, who obtained 2-anthrol from 2-hydroxyanthraquinone by means of hydriodic acid and amorphous phosphorus,

* Much of the aluminium is recovered unchanged.

† It has not been found possible to prepare anthrol with any success by means of zinc dust and aqueous ammonia.

this substance decomposes at about 200°, whereas the product described above became green at 195° and softened at 210°. As this method gives 2-anthrol in good yield and containing little impurity, it has been protected in a preliminary patent specification.

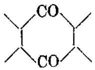
Fraction A.—This product consisted mainly of 3-hydroxyanthranol and was identified by means of its acetyl compound. Occasionally, however, some quantity of dihydroxydianthrone was present and this could be isolated by stirring the mixture with about twice its weight of pure acetone, in which case the 3-hydroxyanthranol alone dissolved.

Summary.

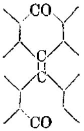
It is shown in this paper that if 2-hydroxyanthraquinone is reduced with zinc dust and ammonia in the manner described, 3 : 3′-dihydroxydianthrone, 3-hydroxyanthranol, and 2 : 2′-dihydroxydianthryl are produced. Although these substances in the order named might be considered to represent distinct steps in the reduction of 2-hydroxyanthraquinone, this scarcely seems to be the case. There is evidence that the first step in the reduction consists in the formation of the 3-hydroxyanthranol and that this is not preceded by the formation of dihydroxydianthrone.

The presence of the latter is to be accounted for by the oxidation of 3-hydroxyanthranol as ammonium salt during the quiescent periods of the reduction process through slight access of air and from the same cause during the introduction from time to time of the ammonia solution. It was observed, for instance, as the results of an experiment not recorded above and in which the reduction was carried out at 100° in a closed autoclave, fitted with a stirrer, that no 3 : 3′-dihydroxydianthrone was formed, and indeed 3-hydroxyanthranol appeared to be the sole product. Again, dihydroxydianthrone was not found to be present, in an experiment in which the reduction was carried out in an atmosphere of hydrogen.

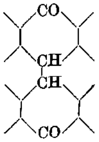
Owing to the cessation of our joint work, evidence as to the origin of the 2 : 2′-dihydroxydianthryl is still uncertain, that is to say, it is doubtful whether it results from the reduction of the dianthrone or of the anthranol or of both. Although such knowledge as we possess points to the dianthrone being at least in part the source of the dianthryl, this is far from conclusive, and the matter, which should not be difficult to determine, must await further investigation. Finally, it is interesting to note that the compounds described in this paper represent complete series of reduction products in the scheme of 2-hydroxyanthraquinone to 2-anthrol. To illustrate these only the *meso*-grouping is given :



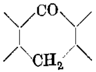
Anthraquinone.



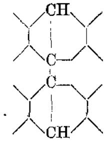
Dianthraquinone.



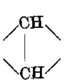
Dianthrone.



Anthrone.



Dianthryl.



Anthrol.

We are indebted to the British Dyestuffs Corporation for the facilities for carrying out this investigation.

CLOTHWORKERS RESEARCH LABORATORY,
DYEING DEPARTMENT,
THE UNIVERSITY,
LEEDS.

[*Received, January* 18*th*, 1922.]

XXXVII.—*Reactions of the Phosphazines.*

By WALTER THEODORE KARL BRAUNHOLTZ.

AN account of some reactions of the phosphineimines, $R_3P{:}NR$, has recently been published (Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861). In the present communication, analogous reactions of the phosphazines are described. The latter compounds, $R_3P{:}N{\cdot}N{:}CR_2$, were first obtained by Staudinger and Meyer (*Helv. Chim. Acta*, 1919, **2**, 619) by the direct union of a phosphine and an aliphatic diazo-compound. It was considered possible that their reactions might proceed similarly to those of the phosphineimines, but that the primary products might in this case readily lose nitrogen and give rise to a variety of substances the preparation of which has hitherto been impossible or very laborious (for example, unsymmetrically substituted ketens, thio-ketens, etc.):

$$R_3P{:}N{\cdot}N{:}CR_2 + X{:}C{:}O \rightarrow R_3P{:}O + R_2C{:}N{\cdot}N{:}C{:}X \rightarrow R_2C{:}C{:}X + N_2$$

The reactions did not, however, proceed in this sense, the liberation of nitrogen either not occurring at all or being accompanied by more complex decomposition. In the case of the reaction between phosphazine and sulphur dioxide, it was possible to isolate a primary additive product.

For a further general consideration of the objects and results of this work, see Staudinger and Braunholtz (*Helv. Chim. Acta*, 1921, **4**, 897).

EXPERIMENTAL.

Triphenylphosphinebenzophenoneazine, $PPh_3{:}N{\cdot}N{:}CPh_2$.

The preparation of this compound from triphenylphosphine and diphenyldiazomethane has been described by Staudinger and Meyer (*loc. cit.*). It forms faintly cream-coloured crystals, m. p. 173° (decomp.).

Behaviour with Carbon Dioxide.—No reaction occurs on passing the gas through a suspension of the phosphazine in cold toluene, or through a solution in boiling toluene. In the latter case, slight decomposition of the phosphazine occurs, but is caused by the heat, since it occurs equally in the absence of carbon dioxide.

Reaction with Phenylcarbimide.—Reaction proceeded readily between equimolecular proportions of the phosphazine and phenylcarbimide, and was exothermic; its course was identical whether the substances were mixed without diluent or in the presence of benzene, toluene, or ether, and it was immaterial whether the reaction was carried out in the air, in carbon dioxide, or in nitrogen. A deep purple coloration was rapidly developed, but was soon replaced by a dark reddish-brown. No nitrogen was evolved. After warming for one hour, the diluent was removed in a vacuum, and the viscous brown residue stirred with ether; part of the reaction products dissolved in the ether, leaving a colourless solid, which, after purification (dissolution in a little benzene and precipitation with light petroleum), gave colourless crystals that melted at 153—154° and did not depress the m. p. of triphenylphosphine oxide. Yield: about 70 per cent. of the theoretical. To the brown, resinous residue from the ethereal filtrate alcohol was added, a brownish-yellow, amorphous solid being obtained. This could not be isolated in a crystalline form or sufficiently pure to furnish conclusive analytical evidence as to its composition; it contained nitrogen but no phosphorus, and analyses and molecular-weight determinations at least suggest that it is a polymeride of the formula $(C_{20}H_{15}N_3)_x$, that is, $(PhN{:}C{:}N{\cdot}N{:}CPh_2)_x$. By repeatedly taking up in ether and precipitating with alcohol, it was obtained as a pale buff-coloured powder melting at 170—175° with previous darkening.

When heated above its m. p., it decomposed with liberation of phenylcarbylamine.

Attempts to isolate the transitory purple product initially formed were unsuccessful, the red residue being always obtained. It is possible that it represents an unstable additive compound between phosphazine and phenylcarbimide, since in the case of phenylthiocarbimide (see below) a similar, but here bluish-green, coloration was transitorily obtained. A second mol. of the carbimide did not enter into reaction with the phosphazine. This reaction therefore probably proceeds as follows :—

$$Ph_3P{:}N{\cdot}N{:}CPh_2 + PhNCO \longrightarrow \left[\begin{array}{l}Ph_3P{-}N{\cdot}N{:}CPh_2\\ \quad\;\; | \quad\; |\\ \quad\;\; O{-}CNPh\end{array}\right] \longrightarrow$$
$$Ph_3PO + (PhNC{:}N{\cdot}N{:}CPh_2)_x.$$

Reaction with Phenylthiocarbimide.—The reaction proceeded less readily than the preceding, but on warming, a transitory deep bluish-green coloration was observed, which soon changed to dark reddish-brown. No nitrogen was liberated. Triphenylphosphine sulphide (m. p. 156—158°; mixed melt test) was obtained in 80 per cent. yield, together with the same pale yellow, amorphous substance as with phenylcarbimide. Only 1 mol. of the thiocarbimide reacted with 1 mol. of the phosphazine, that is, the reaction was quite analogous to the preceding one.

Reaction with Carbon Disulphide.—The phosphazine was suspended in an excess of carbon disulphide. No reaction occurred at room temperature, but on warming under reflux the solid soon dissolved, giving a dark brown solution. After warming for several hours, the mixture was kept over-night, when a crop of straw-coloured crystals of triphenylphosphine sulphide separated. Excess of carbon disulphide in the filtrate was removed in a vacuum and the residue stirred with ether, whereby a further quantity of the phosphine sulphide was obtained. Total yield: 80—85 per cent. of the theoretical. The ethereal solution was evaporated to small bulk and alcohol added; a brown, amorphous solid was thrown out. This was purified as far as possible by repeatedly dissolving in ether and precipitating with alcohol; it was finally yellow and melted with decomposition and previous darkening at 150—156° (Found: C = 81·2; H = 5·0; N = 14·1. $C_{27}H_{20}N_4$ requires C = 81·0; H = 5·0; N = 14·0 per cent.).

The reaction between the phosphazine and carbon disulphide may therefore be written :—

(i) $Ph_3P{:}N{\cdot}N{:}CPh_2 + CS_2 = Ph_3PS + S{:}C{:}N{\cdot}N{:}CPh_2$

(ii) $S{:}C{:}N{\cdot}N{:}CPh_2 + Ph_3P{:}N{\cdot}N{:}CPh_2 = Ph_3PS +$
$Ph_2C{:}N{\cdot}N{:}C{:}N{\cdot}N{:}CPh_2.$

The carbodi-imide derivative was hydrolysed by boiling with concentrated hydrochloric acid, giving benzophenone and hydrazine.

Reaction with Sulphur Dioxide.—The phosphazine dissolved in liquid sulphur dioxide, giving an orange solution which contained the primary additive product. The same product was also obtained as a yellow solid by passing sulphur dioxide through an ethereal suspension of the phosphazine at room temperature. It loses sulphur dioxide gradually on exposure to the air, more rapidly on warming, and also when shaken with cold ether or acetone, the phosphazine being regenerated. The gain in weight accompanying the formation of this product was found to be 14·0 per cent.; $C_{31}H_{25}N_2P,SO_2$ requires an increase of 14·0 per cent.

The reaction between the phosphazine (in benzene solution) and warm sulphur dioxide is complex. Nitrogen was liberated (82 per cent. of the total nitrogen in the phosphazine), and amongst the products triphenylphosphine oxide and sulphide, sulphur, and benzophenone were identified, the last two probably being formed by decomposition of the thionylmethylene derivative, Ph_2CSO, produced as an intermediate.*

Reaction with Thionylaniline.—Equimolecular quantities of the two compounds were warmed together in benzene solution for several hours. The reaction is complex. Nitrogen was liberated (94 per cent. of the total nitrogen in the phosphazine) and triphenylphosphine oxide and sulphide were obtained in approximately equal amounts. In addition, a small quantity of a colourless, crystalline solid and a yellowish-green, oily residue were also produced. The former was soluble in ether or hot alcohol and melted at 168—170°; it contained sulphur but no phosphorus, and decomposed above its m. p. with formation of tetraphenylethylene (mixed melt). The oil was soluble in ether, alcohol, or glacial acetic acid, and insoluble in light petroleum or hydrochloric acid; on attempting to distil it at 12—15 mm. pressure, it decomposed, giving phenylcarbylamine and benzophenone.

Reaction with Diphenylketen.—Equimolecular quantities were brought together in benzene at room temperature, air being carefully excluded. The mixture became feebly warm. No nitrogen

* Professor Staudinger has kindly just informed the author of a recent observation made by him affording support to this view. Sulphur dioxide forms an additive compound with triphenylphosphinediphenylmethylene in the cold, and this also is decomposed, on warming, into triphenylphosphine oxide, benzophenone, and sulphur :—

$$Ph_3P{:}CPh_2 + SO_2 = \begin{matrix} Ph_3P\cdot CPh_2 \\ O\cdot S{:}O \end{matrix} = Ph_3PO + [Ph_2CSO] \longrightarrow Ph_2CO + S.$$

was liberated. After keeping for several hours, triphenylphosphine oxide (66 per cent. of the theoretical) was isolated together with an orange resin which was soluble in all the commoner organic solvents except alcohol and light petroleum, and which could not be purified. On hydrolysis with concentrated hydrochloric acid, this resin gave benzophenone, hydrazine, and a viscous, brown substance which was not identified, but which was probably polymerised keten. These results suggest that the reaction should be written:

$$Ph_3P{:}N{\cdot}N{:}CPh_2 + Ph_2C{:}C{:}O \longrightarrow Ph_3PO + (Ph_2C{:}C{:}N{\cdot}N{:}CPh_2)_x$$

$$\swarrow H_2O$$

$$H_2N{\cdot}NH_2 + Ph_2CO + (Ph_2C{:}C{:}O)_x.$$

Reaction with Nitrogen Peroxide.—Triphenylphosphine oxide was not formed. Amongst the products, which were not further investigated, were found a colourless substance, m. p. 195—198°, insoluble in alcohol, and a buff-coloured product which exploded with great violence at about 80° and was soluble in alcohol.

Ethyl Triphenylphosphineglyoxylate-azine, $PPh_3{:}N{\cdot}N{:}CH{\cdot}CO_2Et$.

The preparation from triphenylphosphine and diazoacetic ester described by Staudinger and Meyer (*loc. cit.*) is improved by mixing the two compounds without a solvent. Small, colourless crystals are obtained, m. p. 113—114°.

Reaction with Phenylcarbimide and with Phenylthiocarbimide.—These reactions proceeded analogously to those already described; the pale yellow, amorphous solid formed at the same time as the phosphine oxide or sulphide did not yield phenylcarbylamine when strongly heated.

Reaction with Carbon Disulphide.—Triphenylphosphine sulphide was obtained (70 per cent. of the theoretical) and a viscous, brown product which was not identified.

Reaction with Sulphur Dioxide.—An additive compound between 1 mol. of the phosphazine and 1 mol. of sulphur dioxide was again obtained in the cold (increase in weight found = 17·2; increase required for $C_{22}H_{21}O_2N_2P,SO_2$ = 17·0 per cent.). With warm sulphur dioxide, nitrogen was evolved and triphenylphosphine oxide and sulphide were formed; glyoxylic ester could not be detected.

Ethyl Triphenylphosphinemesoxalate-azine, $PPh_3{:}N{\cdot}N{:}C(CO_2Et)_2$.

Preparation.—This phosphazine, prepared from triphenylphosphine and diazomalonic ester without a solvent, forms an orange,

treacly mass and has not yet been obtained in a crystalline state. Its identity is proved by its hydrolysis (G. Lüscher, in this laboratory).

Reactions.—The reactivity of the phosphazine towards phenylthiocarbimide and carbon disulphide was practically nil, the initial substances being recovered from the mixture unchanged. With phenylcarbimide intractable, tarry products were obtained, which were not identified.

Triphenylphosphinebenzaldehydeazine, PPh_3:N·N:CHPh.

Preparation.—This compound has not previously been described. It was obtained by adding a saturated ethereal solution of triphenylphosphine to phenyldiazomethane, and forms small, colourless crystals, melting and decomposing at 141—142° (Found: C = 78·4; H = 5·6; N = 7·6. $C_{25}H_{21}N_2P$ requires C = 78·9; H = 5·5; N = 7·4 per cent.).

Hydrolysis.—When heated with aqueous alcohol, triphenylphosphine oxide, hydrazine, and benzaldazine were obtained, the latter two being formed by the decomposition of the benzaldehydehydrazone first produced. The phosphazine is slowly hydrolysed by moist air.

Reaction with Phenylcarbimide and with Phenylthiocarbimide.—The reactions proceeded quite analogously to the corresponding ones with ethyl triphenylphosphineglyoxylate-azine.

The Reaction with Carbon Disulphide was exactly similar to the reaction between carbon disulphide and triphenylphosphinebenzophenoneazine.

The above investigations were undertaken at the suggestion of Professor Staudinger, to whom the author desires to express his thanks for his stimulating interest and invaluable advice. The author's thanks are also due to the Department of Scientific and Industrial Research for financial assistance enabling the work to be carried out.

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XXXVIII.—*The Separation of Miscible Liquids by Distillation. Part II.*

By Arthur Felix Dufton.

In an earlier communication (T., 1921, **119**, 1988) an account was given of a laboratory distillation column which appeared to possess all the advantages sought for in a column for continuous working. A continuous still embodying this column has been constructed, and experiments show that continuous separation of a binary mixture can be conveniently carried out in the laboratory.

A column 1 inch in diameter (Fig. 1) was filled for a length of 200 cm. with thin-walled, cylindrical, glass beads 4 mm. long and 4 mm. in diameter. The cold mixture (of benzene and toluene) was introduced by means of a copper tube lying centrally down the upper half of the column. The rate of flow was regulated by means of a screw valve, a constant-level chamber being provided between the reservoir and the valve. The purity of the products was indicated by means of the ebullioscopes described below. The separated toluene was run off at the bottom, a ball-valve ensuring that a quantity sufficient to cover the heating coil was maintained in the still.

Mercury for a seal over the cork at the bottom of the still was enclosed with a drop of toluene in a small tube. When the still was in use the mercury was expelled and covered the cork, whilst on cooling it was automatically withdrawn into the tube. This facilitated the withdrawal and replacement of the cork.

Loss of heat by radiation was reduced by means of lagging as in the still described in the previous paper.

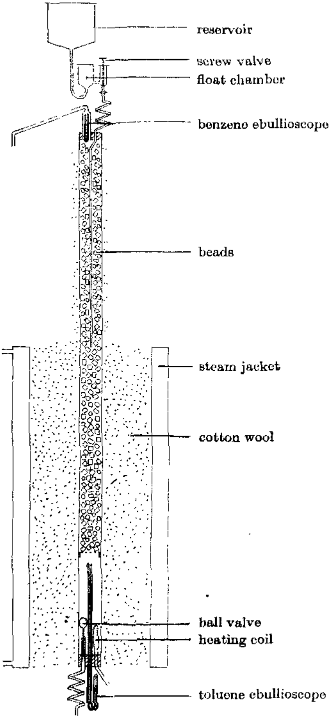
After some experiments to determine the amount of lagging and rate of heating required, the still was in operation for one hour without any adjustment whatsoever, and in this time separated 97·7 c.c. of pure benzene and 100 c.c. of pure toluene from a 50 per cent. mixture. The rate of heating was 800 calories per minute. This corresponds with a thermal efficiency of 38 per cent.

It was found possible slightly to reduce the height of the column, and in an experiment with a column 165 cm. high 62·3 c.c. of pure benzene and 60 c.c. of pure toluene were separated in thirty minutes with a heat supply of 915 calories per minute. This corresponds with an efficiency of 41 per cent.

Note on Ebullioscopes.—In continuous distillation the use of mercury thermometers has the disadvantage that correction for variation of pressure is necessary. A more convenient method of

indicating the purity of a product is afforded by a comparison of the vapour pressure with that of a sample of the desired product

FIG. 1.



at the same temperature. For this purpose, the tension-tube, invented by Chapman Jones (T., 1898, **73**, 175) for the determina-

tion of the boiling point of small quantities of liquid, is well adapted. The tension-tube consists of a small glass U-tube containing mercury. One end contains a drop of liquid and is sealed, whilst the other end is open. Jones pointed out the difficulties of construction and observed that the inclusion of a small bubble of air was necessary to ensure vaporisation and prevent superheating. He made no correction for the partial pressure of this air, although it is appreciable.

In using a tension-tube as an ebullioscope, both the closed end and the open end must be immersed in the saturated vapour of the product. This ensures that the temperature of the liquid in the gauge is that at which the vapour pressure of the product is the pressure at the open end.

The presence of the small bubble of air renders necessary calibration by means of a sample of the desired product. It is convenient to compensate the gauge so that the surfaces of the mercury are level when the product is satisfactory. For a benzene gauge this was effected by using a mixture of benzene with about 2 per cent. of toluene in the gauge and adjusting the amount of mercury during calibration.

The gauge at the bottom of the still was compensated by adjusting the amount of mercury in the open limb so that the lower surfaces were level, as shown in the figure.

The gauges are very sensitive. The admixture of 1 per cent. of toluene with benzene causes a difference in level of 0·85 cm. They are simple to construct, easy to calibrate, and possess the advantage that by means of a platinum wire immediately above the normal mercury surface an electric circuit may be completed immediately a product becomes impure. This circuit may be used to correct the operation of the column or to show on a conveniently placed indicator that the still is not in perfect adjustment.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for funds placed at his disposal which have defrayed part of the cost of this research.

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XXXIX.—*The Hydrogenation of Ethylene in Contact with Nickel.*

By Eric Keightley Rideal.

The catalytic hydrogenation of ethylene in contact with reduced nickel has been studied by Sabatier (*Compt. rend.*, 1897, **124**, 1360) and by D. M. and W. G. Palmer (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 402). The former investigator showed that the reaction would proceed in the presence of carefully reduced nickel and with pure gases at a temperature as low as 30°, accelerating with elevation of the temperature to a maximum rate at about 130—150°. The hypothesis involving the formation of a hydride of nickel is, according to Sabatier, the most satisfactory method of explaining the mechanism of the process of hydrogenation. The investigations of the Palmers revealed the existence of a period of induction varying from several hours at low temperatures to a few seconds at more elevated ones, during which period there was practically no reaction; this period was followed by a rapid increase in reaction velocity rising to a sharp maximum and finally falling rapidly away. No appreciable reaction could be observed below 73°. They advance the hypothesis that hydrogen is preferentially adsorbed, a few ethylene molecules in the adsorption layer act as centres of reaction which develop, finally the catalyst is preferentially covered with a thin layer of ethylene through which the hydrogen has to diffuse for reaction to continue.

Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361), in his studies on the dissociation of hydrogen and on the catalytic combustion of carbon monoxide and hydrogen at platinum surfaces, has shown that the reaction kinetics of these systems can most readily be explained on the assumption that the reactions proceed in a unimolecular film on the catalyst surface. It was deemed of interest to examine the mechanism of the hydrogenation process in more detail, and especially the phenomenon of inductance, in order to investigate how far the phenomena could be interpreted on the hypothesis of adsorption in unimolecular films.

Experimental.

The reaction vessel consisted of a wide glass boiling-tube constricted towards the upper end and connected by means of a three-way tap lubricated with phosphoric oxide to a Sprengel mercury pump, gas burette, and manometer. The capacity of the system

comprising reaction vessel and free space above the manometer was such that 1 mm. of mercury on the gauge at 0° denoted the presence of 106·9 cubic mm. of gas corrected to *N.T.P.* The catalyst consisted of a piece of nickel foil of total area of 6·25 sq. cm. suspended at the centre of the reaction vessel by means of a narrow glass tube containing a thermometer sealed within it. The reaction vessel was wrapped in copper foil to ensure even distribution of temperature prior to insertion in an electrically heated tube furnace.

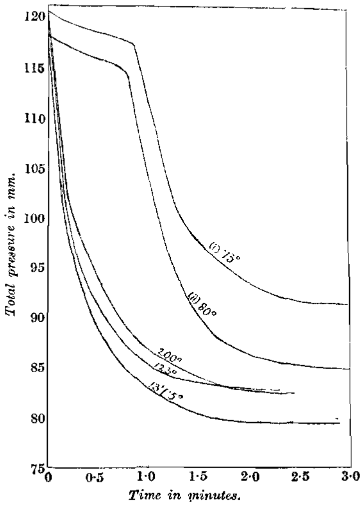
After much preliminary investigation the following method was found to ensure the production of an extremely active and uniform catalytic surface. The nickel foil was immersed in dilute nitric acid, touched with the end of a platinum wire, and withdrawn after contact during a few minutes. It was then carefully dried and the thin film of nickel nitrate slightly decomposed by heating over a hydrogen flame. The catalyst was then placed in the apparatus and the reduction continued in situ, by the admission of hydrogen at low pressures to the reaction chamber. It was found that reaction proceeded rapidly at 270° with liberation of nitrogen and oxides of nitrogen; reduction to a black active nickel, however, did not occur below 340° (compare Taylor and Burns, *J. Amer. Chem. Soc.*, 1921, **43**, 1276). Ignition of the nitrate to the oxide prior to reduction in situ necessitated the employment of a higher temperature for reduction, about 380°, and the catalyst formed in this way was by no means so active. The ethylene was prepared by the action of zinc–copper couples on pure ethylene dibromide and was purified by washing with alcohol prior to solidification by liquid air and fractionation into the storage aspirator. Hydrogen was produced by the electrolysis of potassium hydroxide, all traces of oxygen being removed by passage of the gas over red hot copper. Both gases were stored over water. For experimental purposes various quantities of the two gases, dried by means of soda-lime, were stored in a gas burette over mercury. For each experiment a suitable gas mixture was made up and the reaction chamber evacuated to less than 0·1 mm. pressure. The desired temperature being attained, the dry gas was admitted, the initial pressure recorded, within three seconds after admission of the gas, and the reaction velocity of the reaction followed by recording the diminution of pressure every fifteen seconds. At high temperatures, the gas mixture was warmed prior to admission to the reaction chamber.

Results.—The following conclusions were evident from the experimental data. In pure gases there is no period of induction. It was found that catalysis would proceed uniformly but slowly at low temperatures. At 33°, with a total gas pressure of 124 mm. and a

50 per cent. gas mixture, the rate of diminution of pressure was found to be 0·23 mm. per minute, corresponding with a catalytic rate of combination of 3·84 cubic mm. (reduced to *N.T.P.*) per sq. cm. per minute.

As the temperature was elevated, the reaction velocity increased, the form of the curves plotted from the observed pressure–time relationship being in all cases the same. A few typical curves are shown in the following diagram.

FIG. 1.



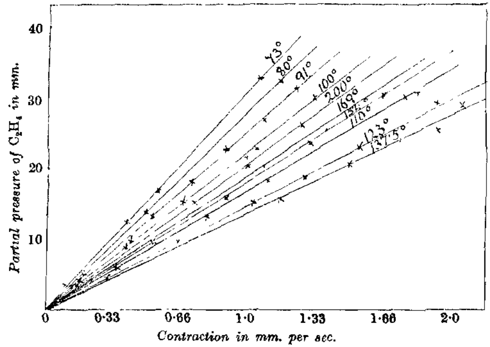
Tangent-derived curves indicating the pressure–velocity relationship revealed the interesting fact that in gas mixtures rich in hydrogen the reaction velocity was at all periods of the reaction strictly proportional to the partial pressure of the ethylene, whilst in mixtures rich in ethylene the reaction velocity was approximately proportional to the hydrogen partial pressure. In both cases, the ethane acts as inert diluent. The influence of the partial pressure

on the reaction velocity of mixtures rich in hydrogen is shown in the following curves (Fig. 2).

Taylor and Burns (*loc. cit.*) have shown that active nickel adsorbs hydrogen only slightly more strongly than ethylene below 110°, but definitely more strongly at higher temperatures under identical gas pressures, and that the quantities adsorbed begin to fall off rapidly at pressures below 200 mm.

In mixtures rich in hydrogen we should expect the surface of the catalyst to be coated with hydrogen. When a space is left by the evaporation of a hydrogen molecule—and at low pressures there will be many such spaces—it may be filled by an ethylene molecule,

FIG. 2.



which then undergoes hydrogenation provided that it is in juxtaposition to an adsorbed hydrogen molecule. The ethane formed appears to act merely as a diluent and consequently possesses but a short life on the catalyst surface or evaporates almost instantaneously. Under these conditions, the reaction velocity will be proportional to the number of ethylene molecules hitting the vacant spaces in juxtaposition to hydrogen molecules and to the shortness of life of the molecules on the surface. At any one temperature the number of ethylene molecules hitting the surface will be proportional to the ethylene partial pressure. For low partial pressures of hydrogen and high ethylene pressures, the converse will be the case and the reaction velocity will at any given temperature be proportional to the rate of contact of hydrogen

molecules or proportional to the partial pressure of this gas. The maximum velocity should be attained when the partial pressure of the two constituents is so adjusted as to ensure the adsorption of the two gases in stoicheiometric ratio. In this respect, the hydrogenation of ethylene is similar to the oxidation of carbon monoxide at a platinum surface investigated by Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1162; *Trans. Faraday Soc.*, 1921, 16), although in this case the adhesion of one reactant, the carbon monoxide, was much greater than that of the oxygen to the platinum surface.

On elevation of the temperature the quantity of hydrogen adsorbed decreases, thus increasing the number of vacant spaces, but the number of ethylene molecules hitting the surface also decreases, but at a slower rate; thus we should expect on elevation of the temperature first a rise and subsequently a diminution in the reaction velocity, as was also noted by Langmuir in the reaction cited above.

The reaction velocities for the ethylene hydrogen reaction at various temperatures are given in the following table.

Mixtures rich in Hydrogen.

Temperature.	Mm. fall of pressure per sec. at 30 mm. partial pressure.	Cubic mm. at *N.T.P.* reacting per sec. per mm. pressure of C_2H_4.
73°	13·6	2·81
80	14·7	2·97
91	16·2	3·17
101	18·5	3·57
110	24	4·53
123	26·7	4·90
137·5	29·8	5·30
154	22·2	3·75
169	21·4	3·50
200	19·7	2·90

For mixtnres rich in ethylene the results were by no means so uniform, the reaction velocity being apparently much less sensitive to temperature changes and only approximating to the values obtained in the hydrogen-rich mixtures at elevated temperatures.

Mixtures rich in Ethylene.

Temperature.	Cubic mm. at *N.T.P.* reacting per sec. per mm. pressure of H_2.
100°	1·96
125	2·69
144	2·69
165	2·75
192	2·94

In the hydrogen-rich mixtures within the temperature range 73° to 137° the relationship between the reaction velocity K in cubic mm. per sec. per mm. pressure of ethylene and the temperature can be expressed in the form

$$\log_{10} K = 2{\cdot}42 - \frac{699}{T},$$

giving a value of 1800 calories per gram-mol. as the heat of the reaction which governs the reaction velocity. Such a small value indicates quite clearly that the limitation to the velocity is not imposed by the rate of evaporation of the hydrogen from the surface, but rather by the length of lives of the reactants on the surface before combination and evaporation.

It is of interest to calculate the efficiency of the catalyst mass. The number of gram-mols. of ethylene, μ, hitting the 6·25 sq. cm. of nickel at a gas pressure of 1 mm. and at $T°$ is given by the equation

$$\mu = \frac{43{\cdot}75 \times 6{\cdot}25}{760\sqrt{28T}},$$

or the number of c.c. of ethylene at $N.T.P. = \frac{8060}{\sqrt{28T}}$.

At 117°, consequently, 81·0 c.c. of ethylene hit the catalyst per second in the absence of any hydrogen. The rate of disappearance of ethylene at this temperature in a hydrogen-rich gas was found to be equivalent to a fall in pressure of 26 mm. in 15 seconds at an ethylene partial pressure of 30 mm. This is equivalent to an ethylene consumption of 4·85 cubic mm. (at $N.T.P.$) at a partial pressure of 1 mm., giving a ratio of 4·85/81,000 or 1 in 16,700. At 137°, when the reaction velocity in a hydrogen-rich mixture was found to be a maximum, 5·30 cubic mm. per sec. disappeared, whilst 75·3 c.c. would have hit the catalyst if no hydrogen had been present. At 200°, 70 c.c. would have hit the catalyst, whilst only 3·00 cubic mm. combined.

It is evident that even at the optimum temperature the rate of combination falls far short of the possible contacts even on the assumption that the hydrogen covers a great deal of the surface and that the activity of the whole surface is not uniform. One of the chief factors in retardation of the reaction velocity is the fact that the collisions of the molecules with the catalyst surface are not elastic. Molecular impact consists in condensation and evaporation. Between these two reactions a definite time interval elapses—the life of the molecule on the surface. At the optimum temperature and in the optimum gas mixture it is assumed that the lives of the hydrogen and ethylene molecules on the catalyst are equal. The

number of effective contacts per second per sq. cm. is given by the expression (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 157)

$$x = 8\left\{\frac{43\cdot75\ N}{760\sqrt{T}}\right\}^2 \cdot \frac{1}{\sqrt{MM^1}} \cdot p^2 \cdot \pi d^2 \cdot \sigma\sigma^1$$

where M, M^1 are the molecular weights, N the Loschmidt number, p the partial pressure in mm. of each constituent (taken equal in this case), d the average molecular radius, and σ, σ^1 the lives of the reactants of the surface in seconds.

The rate of disappearance of the ethylene at 137° and 1 mm. pressure is 5·3 cubic mm. per sec. (at *N.T.P.*) or 0·85 cubic mm. per sec. per sq. cm.

If 1 gram-mol. disappeared per second, this would involve $6\cdot062 \times 10^{23}$ successful contacts per second, hence 0·85 cubic mm. necessitates $2\cdot56 \times 10^{16}$ contacts.

Inserting the values $N = 6\cdot062 \times 10^{23}$, $p = 1$, $\pi d^2 = 10^{-15}$, $\sigma = \sigma^1$, we obtain

$$x = 4\cdot02 \times 10^{26}\sigma^2.$$

Equating these two values, we obtain $\sigma = 8\cdot0 \times 10^{-6}$ sec. as the average life of a molecule of hydrogen and ethylene on the nickel at 410° abs.

One sq. cm. of surface has an area of about 10^{15} molecules, hence if the molecules of hydrogen and of ethylene occupied adjoining squares, the maximum rate of combination in the most favourable circumstances would be $\frac{10^{15}}{2 \times 8 \times 10^{-6}}$ molecules per sq. cm. per sec. or 2·30 c.c. (at *N.T.P.*) per sq. cm. per sec. The actual rate of combination was found to be 0·85 cubic mm. per sq. cm. per sec., indicating a catalytic efficiency of nearly four per ten thousand.

The Period of Induction.

It was noted that when unpurified electrolytic hydrogen was employed in the gas mixture a period of inductance was always obtained. That oxygen will cause this phenomenon was confirmed by the fact that a long or short period of inductance could be obtained by the addition of varying amounts of oxygen to the reaction mixture.

It was noted that during this period of inductance there was a small but gradual diminution of the pressure of the system, indicating that a reaction was proceeding, and that after this period of slow reaction a rapid increase in the reaction velocity occurred (Fig. 1, curves i and ii). Langmuir (*loc. cit.*) has observed a phenomenon precisely parallel to this one in his investigations on the dissociation

of hydrogen at the surface of a hot tungsten wire. In the presence of small quantities of oxygen, no dissociation of the hydrogen takes place until all the oxygen which is selectively adsorbed is removed from the system by condensation of the volatile tungsten oxide on the cold glass surface. After complete removal of the oxygen in this way, the pressure rapidly falls, due to the condensation of the atomic hydrogen produced by the thermal dissociation of the hydrogen, which can now come in contact with the filament. In the process under investigation, the oxygen is selectively adsorbed; having a long life on the catalyst surface, it reacts with the hydrogen to form water, and after removal of all the oxygen in this manner the ethylene undergoes rapid hydrogenation. On the catalyst surface we can imagine the following mechanism of reaction in a hydrogen-rich mixture. On the evaporation of a hydrogen molecule the vacant space may be filled by an oxygen or by an ethylene molecule. The life of the former is very long compared with that of the latter on the surface, consequently the rate of hydrogenation of oxygen is much slower than the hydrogenation of ethylene. The rate of removal of the oxygen will evidently be proportional to the oxygen pressure and inversely proportional to the pressure of the ethylene, the ethylene thus acting as a negative catalyst or

$$\frac{\delta[O_2]}{\delta t} = K\,\frac{C[O_2]}{C[C_2H_4]}.$$

If oxygen be admitted to the system proportionally to the ethylene content, then

$$\frac{\delta[O_2]}{\delta t} = K^1,$$

or $t = K^1[O_2]$, that is, the period of inductance will be proportional to the total quantity of oxygen in the reaction vessel or equal quantities of oxygen will be removed in equal times.

A series of experiments confirmed the above hypothesis, both the ethylene and the hydrogen partial pressures being varied over wide ranges, oxygen being admitted in all cases proportionally to the ethylene content, as is indicated by the following figures.

Ethylene admixed with 0·061 *per cent. of Oxygen.*

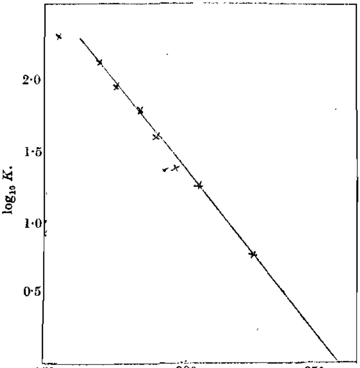
Temperature.	Mm. of H_2.	Mm. of C_2H_4.	$\frac{Mm.}{100}$ of O_2.	Period of inductance in secs.	Time in secs. required to consume one cubic mm. of O_2.
68·8°	86·5	35·5	2·16	82·2	41·2
,,	39·5	17·5	1·07	42	40·2
,,	80	40	2·44	90	40·5

From similar data the following table was compiled.

Temperature.	Time required to consume one cubic mm. of O_2 at *N.T.P.*	Velocity in 10^{-4} c.c. per sec.
45°	545	1·8
55	53·65	18
65	41·75	23·8
68·8	40·5	24
71	40·0	25
75	22·8	43·5
80	15·6	64
90	11·1	90
101	7·2	139
123	5·0	200

If the logarithm of the velocity be plotted against the reciprocal

FIG. 3.



Reciprocal temperature °Abs.

the temperature, the points will be found to lie on a straight ıe, corresponding with the equation

$$\log_{10} K = 8{\cdot}82 - \frac{2538}{T},$$

being expressed in 10^{-6} c.c. per sec.

The slope of the curve indicates that the latent-heat of evapora-on of the hydrogen from the nickel surface is 12,000 cals. per

N*

gram-mol., an indication that there is quite a firm union comparabl to those obtaining in ordinary chemical combinations.

When relatively large quantities of oxygen are added, abou 0·5 per cent., the catalyst undergoes gradual deterioration in cata lytic efficiency, due apparently to the formation of an oxide c nickel which is catalytically inert and cannot be reduced again t the active form below 400°. Evidently oxygen can adhere to th nickel in two distinct ways, one in which it is easily removed b hydrogen at relatively low temperatures, for example, 30° to 200° and one in which it is only removed at very high temperature about 400°, a phenomenon analogous to Langmuir's investigation on the behaviour of oxygen in contact with tungsten and on which throws some light on the investigations of Willstätter an Kelber (*Ber.*, 1921, **54**, [*B*], 1701).

Summary.

The mechanism of the hydrogenation of ethylene at the surfac of reduced nickel has been shown to be capable of explanation o Langmuir's hypothesis of contact action. In excess of hydroger the reaction velocity is proportional to the partial pressure of th ethylene, in excess of ethylene to the hydrogen partial pressure Ethane acts as inert diluent. The optimum temperature is abou 137°. The reaction velocity is governed, not only by the rate o impact of the reactants on the free spaces of the catalyst, but als by the lengths of the lives of the molecules on the surface. Th length of the life of the reactants on the surface at 137° is abou 8×10^{-6} seconds. On the most advantageous conditions of impact the catalytic efficiency of the metal surface is 0·04 per cent. O the admission of oxygen to the reacting mixture, removal of thi gas at a slow rate by hydrogenation occurs, the rate of hydrogena tion being proportional to the partial pressure of the oxygen an inversely to that of the ethylene. This is followed by the muc more rapid hydrogenation of the ethylene. The length of lif of the oxygen molecule on the surface is probably much greate than that of the ethylene. Large quantities of oxygen irreversibl poison the catalyst for low-temperature catalysis, indicating th possibility of the adsorption of this gas by two distinct processes The hydrogenation of oxygen on a nickel surface may be expresse by the equation $\log_{10} K = 8{\cdot}82 - \frac{2538}{T}$, and the heat of evapora tion of hydrogen from the surface is about 12,000 cals. per gram-mo.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY, CAMBRIDGE. [*Received, January 16th*, 1922.]

XL.—*The Colouring Matter of the Scarlet Pelargonium.*

By GEOFFREY SAUNDERS CURREY.

UP to the time when the present work was commenced, our knowledge of the nature of the colouring matter of the scarlet pelargonium (*Pelargonium zonale*) was confined to the variety known as "Scarlet Meteor" (grown in Europe), from the petals of which it was isolated by Willstätter and Bolton (*Annalen*, 1915, **408**, 42). It was shown to occur in the petals, to the extent of 6·6—7·1 per cent. of the dry weight, in the form of an oxonium salt of the diglucoside of pelargonidin, namely, pelargonin (probably pelargonin tartrate). It is also of interest to note that this glucoside was the first of the anthocyanin pigments to be obtained in a crystalline form (Griffiths, *Chem. News*, 1903, **89**, 249). Willstätter and Bolton have also shown (*Annalen*, 1915, **408**, 149) that pelargonin is the colouring matter of the cactus dahlia and the pink cornflower (blue cornflowers contain cyanin in the form of its potassium salt; Willstätter and Everest, *Annalen*, 1913, **401**, 189).

When boiled for a few minutes with 20 per cent. hydrochloric acid, pelargonin yields dextrose and the true, sugar-free pigment, pelargonidin.

Pelargonidin has been obtained synthetically by Willstätter and Zechmeister by the action of trimethoxycoumarin on magnesium anisyl bromide; on treating the product with hydrochloric acid, a tetramethyl ether was obtained, which, on conversion to the free phenolic compound by demethylation, yielded an oxonium salt that proved to be identical with pelargonidin chloride (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 886).

In the present research, it is shown that another variety of *Pelargonium zonale*, namely, "James Kelway" (grown in Australia), contains this same glucoside, *pelargonin*; it occurs in the petals as an oxonium salt of pelargonin to the extent of about 6 per cent. of the dry weight of the petals. The plants from which the flowers were gathered were purchased from Messrs. Shepherd and Sons, of Sydney.

EXPERIMENTAL.

Water Content of the Fresh Petals.

In order to obtain some idea of the water content of the petals, a sample was dried to constant weight at 100°; the loss in weight was found to be 88·27 per cent.

Isolation of the Anthocyanin Pigment.

For the isolation of the pigment, the two methods employed by Willstätter and Bolton were tried, namely, extraction with glacial acetic acid and extraction with 96 per cent. alcohol.

The extraction with glacial acetic acid was carried out by keeping about 200 grams of the fresh petals in contact with this solvent in a closed bottle for a month, with occasional agitation; after filtration, the residue was further extracted with fresh acid for several days and again filtered. To the united filtrates, which had a dark red colour and faint green fluorescence, were added one-tenth of the volume of alcoholic hydrogen chloride (containing 15 per cent. of hydrogen chloride), and then 2 volumes of ether, whereby most of the anthocyanin pigment was precipitated as a reddish-brown mass; after being kept for some hours, the precipitate of *crude anthocyanin chloride was collected, washed with ether, and* dried in the air.

In the second method, 150 grams of fresh petals were extracted with 96 per cent. alcohol in a similar manner to that described above. As observed by Willstätter and Bolton, the extraction was much more complete than with acetic acid; these authors also
state that the alcoholic extract, and the petals lying therein, become
·olorised after having remained for some days. In the present
impa ce, beyond a slight decrease in the intensity of the red colour
by the ›xtract, no such decoloration was observed. It is possible
length of ·idity *of the cell-sap is greater in the petals of this variety*
8×10^{-6} sec·*m* than in those of the variety used by Willstätter and
the catalytic ·nsequently pseudo-base formation is retarded; this
the admission o·ver, not examined.
gas at a slow rate·rom the extracted petals 2 per cent. of alcoholic
tion being proporti·containing 20 per cent. of hydrogen chloride)
inversely to that of ·by 2 volumes of ether, which caused the pre-
more rapid hydrogen·ing matter, as chloride, in the form of a red,
of the oxygen molecule this was collected, washed with ether,
than that of the ethylene
poison the catalyst for ·*ned by both these methods were united,*
possibility of the adsorpti·hort time with methyl alcohol (containing
The hydrogenation of oxyg·hloride), filtered hot to remove insoluble
by the equation $\log_{10} K =$ ·was mixed with one-fifth of its volume
·ric acid; on cooling, the anthocyanin
tion of hydrogen from the sur· masses of slender needles, which were
THE CHEMICAL LABORATORIES·manner, washed with a small quantity
THE UNIVERSITY, CAMBRID·d dried in the air. The bronze-coloured
——·d to be callistephin, a monoglucoside of

pelargonidin, which Willstätter and Burdick obtained from the petals of the purplish-red aster, by reason of the description of its crystalline form given by these authors (*Annalen*, 1916, **412**, 149), but on further examination it was readily seen that this could not be the case.

Identification of the Anthocyanin Chloride.

Crystalline Form.—Hair-fine, red needles, which in bulk form a bronze-coloured mass when dry (Willstätter and Bolton describe their pigment as crystallising in long, thin, red needles) (Found : in air-dried material, loss in a vacuum desiccator at 40 mm. pressure = 8·39 per cent.). Willstätter and Bolton found that pelargonin chloride, when dried in a vacuum over sulphuric acid, lost 10·25 per cent. (= $4H_2O$).

Behaviour with Amyl Alcohol.—In respect to its distribution between aqueous acid and amyl alcohol, the pigment behaves as a normal diglucoside; the distribution number is between 1 and 2 per cent. (the monoglucoside, callistephin chloride, has distribution number 10, and the diglucoside, salvianin chloride, distribution number 50).

Behaviour on Heating.—When heated in a melting-point tube, the anhydrous pigment softens at about 173° and decomposes above 180° (anhydrous pelargonin chloride softens at 175° and melts and decomposes at 180°).

Solubility.—The salt is sparingly soluble in 1—2 per cent. hydrochloric acid in the cold, but dissolves readily on warming, forming an orange-red solution.

The salt is very sparingly soluble in 5 per cent. hydrochloric acid in the cold, but readily in the hot, forming an orange-red solution. It is slightly soluble in water, forming an orange solution which quickly becomes violet (hydrolytic dissociation) and eventually colourless, due to the formation of the pseudo-base. In methyl alcohol it is slightly soluble in the cold and easily on warming, forming a red solution with a green fluorescence (difference from callistephin chloride); on cooling, the chloride crystallises in slender needles. The salt is even less soluble in ethyl alcohol. When a small quantity of the pigment is treated with ethyl alcohol, containing a little hydrochloric acid, the filtrate yields crystals which, under the microscope, appear as stellate clusters of thin, red needles.

When the anthocyanin chloride is boiled with a small quantity of 96 per cent. ethyl alcohol and filtered, the filtrate, on cooling, deposits minute crystals of the basic chloride, which, under the

microscope, appear as small, violet needles displaying a yellow, metallic lustre.

Behaviour with Reagents.—The salt does not develop a coloration with ferric chloride (difference from cyanin chloride), yields a violet precipitate with lead acetate, sodium acetate, or calcium carbonate, develops a violet coloration, changing to greenish-red and finally yellow, with sodium carbonate, sodium hydroxide, or aqueous ammonia, decolorises a solution of sodium hydrogen sulphite, the colour being restored by acids, and very slightly reduces warm Fehling's solution.

With the exception of the crystalline form, these properties are identical with those of Willstätter and Bolton's pelargonin chloride; the anthocyan pigment contained in the petals of the scarlet pelargonium "James Kelway" is, therefore, the diglucoside pelargonin (pelargonidin [1 mol.] + dextrose [2 mol.]).

Hydrolysis of Pelargonin Chloride.

It is stated by Willstätter and Bolton (*Annalen,* 1916, **412,** 133) that if the hydrolysis of pelargonin be carried out under certain prescribed conditions, namely, by careful partial hydrolysis with cold concentrated hydrochloric acid, an intermediate monoglucoside, *pelargonenin,* will be produced. In the present investigation, no attempt was made to obtain this product, as the quantity of pelargonin chloride available was too small. Complete hydrolysis was therefore effected by boiling the glucosidic pigment with 20 per cent. hydrochloric acid for a short time; on cooling, the sugar-free pigment separated in reddish-brown leaflets, which were washed with cold 20 per cent. hydrochloric acid and dried in the air.

Identification of the Anthocyanidin Chloride.

Crystalline Form.—The chloride separates from dilute hydrochloric acid, on cooling, in red tablets.

Solubility.—It is sparingly soluble in cold hydrochloric acid, but dissolves readily when warmed, forming an orange-red or red solution, according to the concentration.

The salt is easily soluble in methyl or ethyl alcohol, forming red solutions with a violet tinge; these solutions are not precipitated by water (difference from cyanidin chloride).

On being shaken with amyl alcohol, an aqueous acid solution of the chloride gives up all the pigment to the alcoholic layer. If the red solution thus formed is shaken with an aqueous solution of an alkali acetate, it will become violet, whilst if shaken with aqueous

sodium carbonate solution, the colour will change to blue and pass completely into the aqueous layer.

The salt dissolves in water without separation of violet flocks (difference from cyanidin chloride), forming a red solution; this is decolorised on warming, the colour being restored by the addition of an acid.

Behaviour with Amyl Alcohol.—The distribution number with respect to amyl alcohol is normal for a non-glucosidic anthocyanin (namely, 100).

Behaviour with Reagents.—The salt does not develop a coloration with ferric chloride (difference from cyanidin chloride), gives a blue precipitate with lead acetate in alcoholic solution, acquires a blue colour with sodium carbonate, and effects the reduction of Fehling's solution to a larger extent than does the glucosidic pigment.

These properties are identical with those of Willstätter and Bolton's pelargonidin chloride.

On account of the small quantity of material available when this research was undertaken, no attempt was made to isolate the yellow sap pigments which may be present in the petals of this variety of pelargonium; this will be made the subject of a later paper.

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XLI.—*Chloropicrin as a Reagent for the Diagnosis of Mercaptans and Potential Mercaptans.*

By Sir Prafulla Chandra Rây and Radhakishen Das.

The reactivity of chloropicrin towards the mercaptans has formed the subject of a previous communication (T., 1919, **115**, 1308). It has been shown that with the typical mercaptans the reaction proceeds as follows

$$3R\cdot SH + NO_2\cdot CCl_3 = (RS)_3C\cdot NO_2 + 3HCl$$

at the ordinary temperature; but at higher temperatures the reaction proceeds further, nitrous fumes being given off from two molecules of the condensed product, thus:

$$>C\cdot NO_2 + O_2N\cdot C< \;\rightarrow\; >C\cdot O\cdot C< + N_2O_3.$$

In the present investigation, mercaptans of divers types have

been similarly treated, and it has invariably been found that there is no deviation whatever from the reaction given above.

When, however, potential or imino-mercaptans, for example, thiocarbamide and its alkyl and aryl derivatives, thioacetanilide, thioacetamide, etc., are employed in place of real mercaptans, the reaction still takes place, but with a marked difference, sulphur being invariably separated and, in some cases, hydrogen sulphide evolved. The reactions under this head may, however, be grouped under two classes :—

1. Those in which there is complete separation of sulphur, for example, thioacetanilide and chloropicrin. During the reaction, copious evolution of hydrogen sulphide takes place with the separation of sulphur and finally of nitrous fumes. The chlorine in the product is partly eliminated by silver nitrate.

In the case of diaryl-substituted thiocarbamides there is complete separation of sulphur, and the product is a trisubstituted guanidine derivative. As guanidine is a strong base, the hydrogen chloride which is produced during the reaction combines with the base, with the formation of the hydrochloride.

When, however, one of the substituents is an alkyl group and the other is an aryl group, the reaction takes a different course. There is complete separation of sulphur as in the above instances, but no guanidine derivative is formed.

2. Those in which two or three molecules of the thio-compound simultaneously take part in the reaction, of which one or two molecules remain intact and simply behave as imino-mercaptans (by tautomerisation), whilst the second or the third molecule, as the case may be, is acted on by one or more atoms of chlorine yielded by the chloropicrin, which, in the process, is disintegrated. In these cases, the sulphur is only partly, not totally, eliminated.

Benzylmethyl- and benzylallyl-thiocarbamides come under the above category. Monomethylthiocarbamide, however, deviates somewhat from the preceding in that the product does not contain non-ionisable chlorine, the halogen being precipitable by silver nitrate.

During the reaction between *p*-chlorophenylthiocarbamide and chloropicrin, nitrous fumes are evolved, that is, the nitro-group is detached; the product has the formula $C_9H_7N_3Cl_2S$. The possibility that the chlorine atom of the chlorophenyl group takes part in its formation is indicated by an independent reaction. When this thiocarbamide is treated with mercuric nitrite, a nitrite free from chlorine of the empirical formula $C_7H_6O_5N_4S_2Hg_3$ is obtained, which may be graphically represented as

$$NO_2Hg{\cdot}S{\cdot}C_6H_4{\cdot}NH{\cdot}C(:NH){\cdot}S(:HgO){\cdot}HgNO_2.$$

Thioacetamide, as also thiobenzamide, presents some peculiarities. Here three molecules take part in the reaction, but only one atom of sulphur is detached; sulphur is liberated and hydrogen sulphide is formed. The latter reduces the nitro-group to the amino-group, and the final product has the formula $C_7H_{14}N_4S_2$.

The evidence afforded by ethylenethiocarbamide is very interesting. This compound may be regarded as derived from 2-thiol-4 : 5-dihydrothiazole by the substitution of NH: for S; but whilst the latter behaves like a real mercaptan (see Expt. 3), the former would seem to belong to the ketonic variety, that is, it is a potential mercaptan. Sulphur separates, hydrogen sulphide is formed, and the nitro-group is reduced to the amino-group, the product haviug the formula $C_6H_{11}N_4ClS$.

EXPERIMENTAL.

Potassium Salt of 2-Thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and Chloropicrin.

The reaction at 50° has already been described (T., 1919, **115**, 1311); when it proceeds at 100°, nitrous fumes are evolved, and by the condensation of two molecules of the substance $C_{25}H_{15}O_2N_7S_9$ (*loc. cit.*), the compound $(C_{25}H_{15}N_6S_9)_2O$ is obtained along with the previous one of m. p. 129°. The ether is extracted from the mixture with boiling methyl alcohol and purified by recrystallisation; it melts at 106—107° (Found: C = 43·02; H = 3·67; S = 41·74. $C_{50}H_{30}ON_{12}S_{18}$ requires C = 43·17; H = 2·16; S = 41·44 per cent.).

Potassium Salt of 2 : 5-Dithiol-1 : 3 : 4-thiodiazole and Chloropicrin.

The reaction at 100° has already been described (*loc. cit.*, p. 1312). At the room temperature (30°), the reaction does not proceed so far that nitrous fumes are evolved with formation of the ether $C_8ON_6S_9$. The product, after crystallisation from alcohol, melts sharply at 152° (Found: C = 16·98; N = 19·52; S = 51·34. $C_8O_4N_8S_9$ requires C = 17·14; N = 19·99; S = 51·43 per cent.).

2-Thiol-4 : 5-dihydrothiazole and Chloropicrin.

The components were heated in alcoholic solution under reflux for four hours. On cooling, no separation of sulphur took place. The filtered solution was concentrated, and the crystalline mass obtained was recrystallised from alcohol, when white crystals,

m. p. 95°, were deposited (Found: N = 13·21; S = 46·84. $C_{10}H_{12}O_2N_4S_6$ requires N = 13·59; S = 46·60 per cent.).

Potassium Salt of Dithioethylene Glycol and Chloropicrin.

The potassium salt was dissolved in alcohol and chloropicrin added drop by drop at the ordinary temperature. A violent reaction ensued, the temperature rose rapidly, and a yellow mass began to separate; copious evolution of nitrous fumes also took place. The mixture was heated under reflux to complete the reaction, and the yellow mass obtained on cooling was filtered, washed with alcohol, dried, and triturated with water; the aqueous filtrate contained potassium chloride. After drying, the yellow mass was crystallised from hot nitrobenzene and obtained as a yellow powder sintering at 120° and melting at 123°. In this case free sulphur was proved to be absent.

In another experiment, the reaction was allowed to take place at 0°. In this case also, nitrous fumes were evolved and the same product was obtained (Found: C = 28·14; H = 4·80; S* = 65·57. $C_{14}H_{30}OS_{12}$ requires C = 28·09; H = 5·02; S = 64·21 per cent.).

Pinacolylthiocarbamide and Chloropicrin.

The parent substances in alcoholic solution were heated under reflux for four hours. No separation of sulphur took place. The reaction mixture, after filtration and subsequent evaporation, yielded an oil which could not be made to solidify (Found: C = 43·01; S = 16·59; Cl = 8·91. $C_{15}H_{26}O_2N_5ClS_2$ requires C = 44·10; S = 15·80; Cl = 8·71 per cent.).

Ethyl Mercaptan and Chloropicrin.

The components in alcoholic solution did not react when heated under reflux or in a sealed tube at 100°. When the temperature was raised to 220—240°, a minute quantity of a white substance was formed, which was not soluble in carbon disulphide, proving that sulphur had not been eliminated. As the product could not be obtained pure, no definite composition could be assigned to it.

Potential Mercaptans.

p-*Chlorophenylthiocarbamide and Chloropicrin.*

The reacting substances in alcoholic solution were heated under reflux for five hours. Nitrous fumes were evolved and sulphur

* Sulphur was estimated by fusion with potassium nitrate and sodium carbonate; hence a slightly high percentage of sulphur was sometimes found.

separated. The mother-liquor, on concentration, gave white crystals, which were washed with carbon disulphide and recrystallised from alcohol; the product melted at 245—246° (Found: C = 42·33; Cl = 28·22; S = 11·90. $C_9H_7N_3Cl_2S$ requires C = 41·53; Cl = 27·31; S = 12·31 per cent.).

The compound obtained from *p*-chlorophenylthiocarbamide and mercuric nitrite had the formula $C_7H_6O_5N_4S_2Hg_3$ (Found: C = 9·26; H = 1·64; N = 5·87; Hg = 67·37; S = 7·24. Calc., C = 9·44; H = 0·67; N = 6·29; Hg = 67·42; S = 7·19 per cent.).

Thiocarbanilide and Chloropicrin.

The components in alcoholic solution were heated under reflux for three hours. The liquid assumed a yellow colour and sulphur separated. After being cooled, filtered, and concentrated, the alcoholic mother-liquor yielded a semi-solid mass, which was washed with ether to remove tarry matter and with acetone; the slightly discoloured, white residue, after recrystallisation from hot water, formed glistening, white crystals, m. p. 252° (Found: C = 69·76; H = 6·75; N = 13·23; Cl = 11·18. $C_{19}H_{18}N_3Cl$ requires C = 70·47; H = 5·56; N = 12·98; Cl = 10·97 per cent.).

s-*Ditolylthiocarbamide and Chloropicrin.*

The method of preparation and purification was the same as in the previous case. The product melted at 230° (Found: C = 72·38; H = 7·06; Cl = 10·12. $C_{22}H_{24}N_3Cl$ requires C = 72·23; H = 6·57; Cl = 9·71 per cent.).

The reaction between chloropicrin and the following compounds in alcobolic solution has also been investigated. Sulphur separated in every case: in addition, with thioacetanilide nitrous fumes were evolved, and with thioacetamide hydrogen sulphide was produced. The products are evidently complex, and their precise nature has not yet been determined. They are as follow: from methylthiocarbamide, a hydrochloride, colourless, shining crystals, m. p. 222° (Found: C = 25·53; H = 6·70; Cl = 19·10; S = 17·19; N = 29·99. $C_4H_{11}N_4ClS$ requires C = 26·3; H = 6·03; Cl = 19·45; S = 17·54; N = 29·90 per cent.); from allylthiocarbamide, a golden-yellow oil (Found: C = 38·39; Cl = 13·79; S = 12·58. $C_8H_{12}O_2N_3ClS$ requires C = 38·48; Cl = 14·20; S = 12·80 per cent.); from henzylallylthiocarbamide, an oil (Found: C = 57·33; H = 6·91; Cl = 9·64; S = 8·11. $C_{18}H_{20}O_2N_3ClS$ requires C = 58·53; H = 5·13; Cl = 9·11; S = 8·22 per cent.); from

benzylmethylthiocarbamide, a substance, m. p. 176—177° (Found: C = 56·56; H = 6·20; S = 8·81. $C_{17}H_{18}O_2N_3ClS$ requires C = 56·27; H = 4·97; S = 8·82 per cent.); from ethylenethiocarbamide, a substance crystallising in plates, m. p. 270° (Found: C = 34·79; H = 6·40; N = 27·07; Cl = 17·95; S = 15·98. $C_6H_{11}N_4ClS$ requires C = 34·87; H = 5·33; N = 27·12; Cl = 17·19; S = 15·50 per cent.); from thioacetamide, colourless, silky needles, m. p. 103° (Found: N = 25·62; S = 29·56. $C_7H_{14}N_4S_2$ requires N = 25·69; S = 29·36 per cent.); from thiobenzamide, a substance, m. p. 88° (Found: C = 66·01; H = 4·60; N = 13·20; S = 16·87. $C_{22}H_{20}N_4S_2$ requires C = 65·34; H = 4·97; N = 13·86; S = 15·85 per cent.); from phenylallylthiocarbamide, a golden-yellow oil (Found: C = 68·55; N = 11·13; Cl = 14·61. $C_{14}H_{17}N_2Cl$ requires C = 67·59; N = 11·27; Cl = 14·29 per cent.); from thioacetanilide, colourless, shining plates, m. p. 186—187° (Found: C = 54·03; H = 6·71; N = 11·38; Cl = 28·30. $C_{11}H_{14}N_2Cl_2$ requires C = 53·87; H = 5·71; N = 11·42; Cl = 29·00 per cent.); from thiocarbamide, an oil.

Summary.

Seventeen typical thio-compounds have been subjected to investigation. Of these, five are known to be real mercaptans, and the rest as potential ones. In not a single instance has it been found that there is separation of sulphur in the case of real mercaptans, whereas sulphur is either partly or completely eliminated from the potential ones. Chloropicrin may, therefore, be safely used as a reagent for the diagnosis of mercaptans and potential mercaptans respectively.

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XLII.—*The Nitration of* m-*Nitrotoluene.*

By OSCAR LISLE BRADY.

IN a note on the nitration of toluene, Giua (*Gazzetta*, 1921, **51**, ii, 113) takes exception to a statement made by Taylor and myself (T., 1920, **117**, 876) and repeated by Drew (T., 1920, **117**, 1615) to the effect that Molinari and Giua (*Z. ges. Schiess-u. Sprengstoffw.*, 1914, **9**, 239) considered that the trinitrotoluene they isolated

from the oily residues obtained in the purification of commercial trinitrotoluene and melting at 79·5°, was the 2 : 3 : 6-compound. Giua points out that although there was some suggestion at that time that it might be this, then unknown, isomeride, or else 2 : 3 : 5-trinitrotoluene, this view was subsequently abandoned. In his book " Chimica delle sostanze esplosive " (1918), he follows Will (*Ber.*, 1914, **47**, 704) in considering that only the 2 : 4 : -6, 2 : 3 : 4-, and 2 : 4 : 5-trinitrotoluenes are formed in the nitration of toluene, and he now accepts the suggestion of Taylor and myself (*loc. cit.*) that the substance melting at 79·5° was an additive compound of 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes. It is due to Professor Giua to explain that reference was made to the early paper as containing the first mention of the possibility of the presence of 2 : 3 : 6-trinitrotoluene in the nitration products of toluene, and that it was not the intention of the authors to convey the impression that the statement referred to represented his present views.

Drew (*loc. cit.*) showed that Will's conclusions that 2 : 3- and 2 : 5-dinitrotoluenes gave on nitration only the 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes respectively were not correct, as the 2 : 3 : 6-(or 2 : 5 : 6-)isomeride is also produced in each case. Giua contests the accuracy of these results without, however, adducing further experimental evidence. Drew employed in the separation, hydrazine hydrate, which acted more readily on the 2 : 3 : 4- and 2 : 4 : 5-isomerides and removed them as dinitrotolylhydrazines. Giua questions the soundness of this method and maintains that since 2 : 3 : 6-trinitrotoluene also contains, from theoretical considerations, a mobile nitro-group, it would react with hydrazine hydrate; further, because 2 : 3 : 4-trinitrotoluene reacts but slowly compared with the 2 : 4 : 5-compound with *p*-aminoacetophenone, he assumes without experimental verification that it would not react very readily with hydrazine hydrate, and suggests therefore that Drew's compound was probably the 2 : 3 : 4- (m. p. 112°), and not the 2 : 3 : 6-trinitrotoluene (m. p. 111°), although Drew found that it did not depress the melting point of the latter.

It has already been pointed out by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) that 2 : 3 : 6-trinitrotoluene behaves abnormally with ammonia and that the 3-nitro-group is not so readily replaced as might be expected, and Bowman and myself (T., 1921, **119**, 894) commented on the abnormal behaviour of this compound with hydrazine hydrate. Giua (*Gazzetta*, 1919, **49**, ii, 166) and Bowman and myself have shown that hydrazine hydrate reacts with 2 : 3 : 4- and 2 : 4 : 5-trinitrotoluenes to give the corresponding dinitrotolylhydrazines.

In order to decide the point at issue, a number of further experiments have been made. The action of hydrazine hydrate with one molecular proportion of the three isomerides in cold alcoholic solution has been studied. In the case of the 2 : 3 : 4- and 2 : 4 : 5-compounds, within half-an-hour a large precipitate of the dinitrotolylhydrazine had formed, in the case of 2 : 3 : 6-trinitrotoluene no precipitate had formed, and on acidifying and diluting the solution almost the whole of the nitro-compound was recovered unchanged. *m*-Nitrotoluene was nitrated to the mixture of 2 : 3-, 2 : 5-, and 3 : 4-dinitrotoluenes (compare Brady and Gibson, T., 1921, **119**, 99), and as much as possible of the 3 : 4-dinitrotoluene frozen out (Sirks, *Rec. trav. chim.*, 1907, **27**, 208), as this cannot yield the 2 : 3 : 6-trinitrotoluene. The remaining oil was trinitrated and after washing allowed to crystallise. The mixture of trinitrotoluenes obtained in this way and consisting mainly of the 2 : 3 : 4- and 2 : 4 : 5-compounds was washed with cold alcohol to remove the eutectic of 2 : 3 : 4-, 2 : 4 : 5-, 2 : 3 : 6-trinitrotoluenes and unchanged dinitrotoluenes. Part of the alcoholic solution was evaporated and the oil re-nitrated to ensure absence of unchanged dinitrotoluenes, and 5 grams of the mixture thus obtained were dissolved in 100 c.c. of warm alcohol and the solution was cooled to 30°, when 2·5 grams of a 50 per cent. aqueous solution of hydrazine hydrate diluted with 10 c.c. of alcohol were added. A deep red coloration occurred which slowly lightened, red crystals beginning to separate, and the temperature rose to 32°. After thirty minutes, the mixture was filtered, and the filtrate, on leaving for an hour, deposited yellow crystals which under the microscope were found to consist of almost colourless crystals mixed with the characteristic red crystals of the dinitrotolylhydrazine. On crystallisation from alcohol, almost colourless crystals were obtained of what was undoubtedly 2 : 3 : 6-trinitrotoluene (Found : N = 18·7. Calc., N = 18·5 per cent.). This melted, alone, at 110—111°, mixed with 2 : 3 : 4-trinitrotoluene (m. p. 112°), at about 80°, and mixed with a specimen of 2 : 3 : 6-trinitrotoluene prepared synthetically, at 110—111°. The compound gave identical colour reactions with acetone and ammonia, and acetone and sodium hydroxide as the 2 : 3 : 6-trinitrotoluene, which are quite distinct from those of the 2 : 3 : 4-isomeride. By diluting the mother-liquor from the first crop of crystals, a further quantity was obtained rather badly contaminated with dinitrotolylhydrazine. The latter compound can be removed as a soluble nitrate by treating the crystals with cold 70 per cent. nitric acid, and diluting. In the separation it is necessary to ensure that there is not an excess of hydrazine hydrate, which at higher temperatures reacts

with the 2 : 3 : 6-trinitrotoluene, but it seems that in a mixture of the three isomerides the 2 : 3 : 4- and 2 : 4 : 5-compounds react preferentially with the reagent.

Separation of 2 : 3 : 6-trinitrotoluene has also been achieved by treatment of the mixture with aqueous sodium sulphite for a limited period and recrystallising the residue three times from alcohol.

Although the method of separation employed above differs in some details from that of Drew, his contention is confirmed that 2 : 3 : 4-, 2 : 4 : 5-, and 2 : 3 : 6-trinitrotoluenes are formed by the nitration of *m*-nitrotoluene.

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XLIII.—*The Use as a Drying Agent of Phosphoric Oxide treated with Ozone.*

By JOHN JOB MANLEY.

DURING some preliminary experiments with two McLeod gauges constructed for measuring very small gas pressures, it was found necessary to direct special attention to the way in which phosphoric oxide used as the drying agent comported itself. The problem, at first sight comparatively simple, proved on investigation to be difficult of solution; the difficulty arose, not from any intrinsic cause, but was rather the result of an intimate association of the problem with two others of a cognate nature to be dealt with in a further communication.

It is well known that by distilling phosphoric oxide in the presence of oxygen and spongy platinum,[1] a product having a very high degree of purity may be obtained, but the process is admittedly lengthy, tedious, and costly; and this is markedly so when considerable quantities are required; moreover, it is by no means easy to obtain the purified compound in the light, powdery form so essential for perfect and rapid drying. But when phosphoric oxide is used for drying gases, it need not be *chemically* pure; the requirements of the physicist are fully met if two conditions are complied with. (1) The oxide must be free from all substances having measurable vapour pressures; and (2) impurities which, by reacting with water or mercury vapour or with the gas

that is being dried, give rise to gaseous matter of a kind other than that which is under observation must be removed or changed into harmless products.

In order to investigate the matter somewhat fully, samples of the purest phosphoric oxide obtainable were at various times purchased from different firms. All the samples were found to contain phosphorous oxide. In six samples the amount varied within the limits of 0·43 and 1·06 per cent.; but a seventh sample (α) was so nearly free from phosphorous oxide that, when tested, many hours elapsed before a faint cloud of mercurous chloride appeared, and on evaporating an aqueous solution, no hydrogen phosphide was detected. Four of the samples were chosen for comparative experiments, but before the experiments were carried out three of the samples were purified. One (K_1) was distilled in the presence of oxygen and spongy platinum; two others (K_2, K_3) were freed from injurious impurities by the method described below; the fourth (α), containing the trace of phosphorous oxide already alluded to, was used as received.

Purification of the Samples K_2 and K_3.—These two samples were rendered eminently suitable for drying gases by proceeding as follows:—

A U-tube (subsequently used as a drying chamber) was loosely filled with the oxide, and the inlet and outlet tubes were lightly plugged with asbestos fibre; the U-tube was then set up within a small air-bath, and an ozone generator was attached. Next, the temperature of the bath was slowly increased while a continuous stream of air, previously freed from aqueous vapour and carbon dioxide and powerfully ozonised, was passed through the charged tube. During this period the escaping gas was frequently tested with potassium iodide and starch, and when it was found to be highly and continuously charged with ozone at the temperature of 300° or rather more, it was concluded that the purification of the oxide had been accomplished. The behaviour of the impurities in the two samples may here be noted.

Sample K_2.—At all temperatures below 160° there was no appreciable diminution in the quantity of the escaping ozone, but from that point upwards the presence of ozone became less and less marked until, at 175°, it was entirely lost. On temporarily reducing the temperature to 170°, traces of ozone were again detectable. The temperature of the bath having again been raised to the higher value of 175°, a continuous stream of ozonised air was maintained. After the expiration of twenty-five minutes, the indicator showed that ozone had reappeared in quantity, and it was therefore concluded that some impurity (P_4O_6 ?) had now

been fully oxidised. At this stage of the experiment a white, crystalline deposit was observed in the projecting part of the tube, and this on analysis proved to be pure phosphoric oxide. Whenever phosphoric oxide, rendered impure by the lower oxide, is treated in the way described above, similar deposits are invariably produced, and the more marked the impurity the greater is the quantity of the crystalline deposit. Finally, on raising the temperature of the bath, it was found that throughout the whole range 175—303° ozone freely escaped from the heated oxide; whence it appears that all oxidisable impurities were completely satisfied with oxygen at the lower temperature of 175°. The purified compound was subsequently examined for phosphorous oxide; its aqueous solution remained for hours quite unaffected both by silver nitrate and also by mercuric chloride.

Sample K_3.—This sample contained foreign matter calculated as 0·43 per cent. of phosphorous oxide. When heated with ozone, the behaviour of K_3 differed from that shown by K_2. Three distinct stages of oxidation were noted; these occurred within small ranges of the respective temperatures 147°, 197°, and 220°. Each stage, although of brief duration, was sbarply defined.

This second purified sample, when examined for phosphorous oxide, was, like K_2, found to be free from that impurity.

The oxidation of impurities as outlined above is easily effected, and the method involves but little attention or skill. The phosphoric oxide retains its loose, bulky form, and, other conditions being equal, a gas in contact with it is therefore most quickly dried. Also there is the added advantage that the purified compound, being already in situ, is not subsequently and of necessity exposed to the dampness of the air. To determine their efficacy as drying agents, the four samples of oxide were severally examined as follows.

Sample α.—A drying chamber was charged with the oxide and then fused to a tube leading to a Sprengel pump and afterwards highly exhausted, and in order to effect a very complete removal of aqueous vapour from the internal surfaces, some weeks were allowed to pass before accurate measurements of the gas pressure were made, but during this period the pump was almost daily used.

When the oxide had been in the apparatus for fourteen weeks, the gas (air) pressure was reduced until the value as determined by the attached McLeod gauge was 0·00017 mm., then, leaving the pump at rest, measurements of the steadily growing gas pressure p were carried out during successive days. On the ninth day, $p = 0·00181$ mm.; the increase in p was therefore 0·00174 mm., a mean daily rate of 0·00019 mm. After the conclusion of the

first series of observations, the pump was again brought into frequent use during another five weeks, and then a second series of daily pressure readings carried out. Starting with $p = 0{\cdot}00041$ mm., the value had by the eighth day become 0·00133 mm., the difference being 0·00092 mm., which equals a mean daily rate of 0·000115 mm. Proceeding as before and making frequent use of the pump during an additional seventeen weeks, a third and final series of observations, also extending over eight days, was obtained. In this last series of experiments with sample α, the initial and final values of p were respectively 0·00068 and 0·00123 mm.; the growth in p was therefore 0·00055 mm., and this equals a mean daily rate of 0·00007 mm. The final rate observed is 2·5 times smaller than that obtained in Series II.

Samples K_2 and K_3.—The chambers containing these two samples of purified oxide were fused to separate pumps, and high vacua produced and maintained within them for many weeks; then, leaving the pumps at rest, the residual air pressures, p, were measured once on each of nine successive days. It was thus found that the mean daily growth in p equalled 0·000031 mm. for K_2, whilst that for K_3 was 0·000034 mm.

Concluding experiments, calculated to throw light on the behaviour of sample α as recorded above, were at this juncture carried out with phosphorous oxide newly prepared by Thorpe and Tutton's method; these I now describe.

Phosphorous Oxide.—A drying chamber was charged with the oxide and fused to the pump, which still retained the purified phosphoric oxide K_3, and the whole apparatus was exhausted as rapidly as possible. The fall-tube of the pump was quickly stained, and in consequence of this the reduction of the gas pressure p was a matter of difficulty, and some twenty hours elapsed before the clicking sound so characteristic of the approach to a high vacuum was heard. On arresting the action of the pump at any time during the first days of the experiments, p increased with abnormal rapidity, and this fact suggested that a continuous formation of gas was taking place. Exact measurements made after the expiration of three days showed that p was increasing at the mean daily rate of 0·0166 mm. By using the pump freely during a period of six weeks, this rate was reduced to 0·004 mm., and similarly during an additional two weeks, the mean daily rate was reduced to the small value of 0·00038 mm.

Before discussing the results, I would disarm possible criticism by reminding chemists that no claim is here put forth for chemical purity; those desiring "chemically pure" phosphoric oxide will set about the task of preparing it in some other way. The point

which I desire to stress is that although in this instance chemical purity of the highest degree was not attained, we yet do by the method adopted for purifying samples K_2, K_3 secure possession of phosphoric oxide the purity of which is such that when the substance is used for drying hydrogen, oxygen, nitrogen, air, or helium (all of which have been critically tested during the past ten or twelve years), no measurements of a purely physical character subsequently conducted with those gases are in the least degree likely to be affected; and this being so, phosphoric oxide purified by ozone fulfils in each of the cases cited above the requirements of the physicist.

We have seen that, in the presence of phosphorous oxide, reduction in the pressure of a gas is difficult; and that with the attainment even of a moderately high vacuum, on bringing the pumps to rest, the growth in the pressure p acquires an abnormally high rate, and, further, that although this rate decays, it persists for weeks. The exceptional increment for p is, however, understood when we remember that the interaction of aqueous vapour and *finely divided* phosphorous oxide such as we used results in the ready formation of hydrogen phosphide. Now the formation of this gas proceeds at the greatest rate when the aqueous vapour present is a maximum quantity, that is, during the earlier stages of drying. With the complete removal of aqueous vapour by phosphoric oxide, the production of hydrogen phosphide necessarily terminates, and so from this time forth the attainment of a high vacuum is a possibility. But since the boiling point (173°) of phosphorous oxide is not high, the vapour pressure even at the ordinary temperature must be appreciable, and therefore when the lower oxide is present in the drying chamber, it will be impossible to establish vacua of the highest order. The truth of these remarks receives confirmation from the results of the experiments with sample α cited above. But in addition to the disturbing factor introduced by hydrogen phosphide, a secondary and one of even more importance arises from the appearance of free hydrogen An analysis of the dark substance removed from the fall-tube of the Sprengel pump revealed the powder as mercury phosphide; this substance was in all probability formed in accordance with the equation

$$2PH_3 + 3Hg = 3H_2 + Hg_3P_2.$$

It therefore follows that during the reaction between hydrogen phosphide and mercury there were substituted 3 vols. of hydrogen for 2 vols. of hydrogen phosphide, and in consequence of this the pressure was still further augmented.

In confirmation of the above interpretations, the following two experiments are cited.

Experiment 1.—After the whole apparatus had been cleaned, dried, and exhausted, a very small quantity of hydrogen phosphide, obtained from pure phosphonium iodide and subsequently purified and dried, was introduced. Using the McLeod gauge as though we were about to measure a gas pressure, the bulb and most of the capillary tube were charged with mercury; the cistern was then lowered and when the mercury had left the gauge the whole interior surface was found to be covered with a highly uniform film having a golden tint; this film extended upwards within the capillary tube to the highest point reached by the mercury, but not beyond. From the conditions under which the film of mercury phosphide was formed it was concluded that electrical charges, produced by the friction between the mercury and the glass, initiated the chemical change. Holding this view, I was led to try the following experiment.

Experiment 2.—A clean dry tube was charged with pure mercury and set up as a barometric column; some hydrogen phosphide, prepared as for experiment 1, was then introduced, and the volume of the gas under normal temperature and pressure determined. A clean iron wire having been passed up through the column of mercury, the upper end of the tube was fitted with a tin-foil cap; the wire and the cap were then joined to an induction coil, and a glow discharge was set up within the hydrogen phosphide. The volume of the gas at once began and continued to increase steadily, and at the same time a golden, iridescent film appeared within the tube; the general appearance of this film was similar to that of the film obtained in the McLeod gauge during experiment 1. When the volume of the gas had increased by 15 per cent., the tube was pierced by the discharge and the experiment abruptly terminated, but as the available evidence was now sufficiently complete, no repetition of the experiment was required. The film, when subjected to analysis, was found to be, as expected, mercury phosphide.

On reviewing our data in the light of the evidence adduced, it is at once apparent that although the sample of oxide α contained but a mere trace of phosphorous oxide, yet even so its quality as a drying agent was markedly affected, and when the oxide was finally tested after a lapse of thirty-six weeks, the daily growth in the pressure on arresting the action of the pump was still some ten times greater than would probably have been the case if the oxide had previously been treated with ozone.

With regard to the two samples, K_2, K_3, which had been sub-

jected to the influence of ozonised air, their superiority over the unpurified sample of oxide α is at once revealed by comparing the respective data (*vide supra*) for the three several samples. Contrasted with phosphoric oxide purified by distillation in oxygen, the ozonised oxide is sometimes found to absorb aqueous vapour more rapidly than the sublimed compound; this, however, appears to happen only when the latter in condensing forms a somewhat compact mass with a more restricted surface; apart from this, the two modes of purification yield phosphoric oxide identical in merit as drying agents.

In conclusion, it may be remarked that as the various experiments were comparative and differential rather than absolute, the slight effect on the increment in the pressure p following an attenuation of the gas skins upon the internal surfaces of the apparatus has not here been taken into account; such a course being obviously unnecessary.

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XLIV.—*The System Ferric Oxide—Sulphuric Acid—Water.*

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THE sulphates of ferric iron—acid, normal, and basic—have been the subject of many investigations. The normal sulphate occurs naturally as the mineral coquimbite, and several different mineral basic sulphates have been described, of which the following may be mentioned :—

Mysite, $2Fe_2O_3,5SO_3,12H_2O$ (Moissan, "Traité de Chim. Min.," IV, 375).

Fibroferrite, $3Fe_2O_3,5SO_3,27H_2O$ (Rose, *Pogg. Ann.*, 1832, **27**, 315).

Apatelite, $3Fe_2O_3,5SO_3,2H_2O$ (Meillet, *Ann. Min.*, 1841, **3**, 808).

Raimondite, $2Fe_2O_3,3SO_3,7H_2O$ (Breith, *Berg. Hut. Ztg.*, 1866, **25**, 149).

Illohmanite, $2Fe_2O_3,3SO_3,15H_2O$ (Moissan, "Traité," IV, 375).

Carphosiderite, $4Fe_2O_3,5SO_3,13H_2O$ (Breith, *Sch. J.*, 1827, **50**, 314).

In addition, stoicheiometric formulæ have been given to a very large number of reaction products, such as those which separate

from commercial "nitrate of iron" mordant in the absence of sufficient free acid. Cameron and Robinson (*J. Physical Chem.*, 1907, **11**, 641) have shown that products obtained in this way have little claim to rank as chemical individuals, since they are mixtures the composition of which depends on the exact conditions of their preparation.

Investigating the system Fe_2O_3–SO_3–H_2O by the Schreinemakers "rest" method, which alone is able to give certain information as to the composition of the solid phases, Cameron and Robinson were unable to obtain evidence of the existence of any definite basic ferric sulphate, all the products on the basic side being solid solutions of ferric oxide (or hydroxide) in the normal sulphate or perhaps in a crystalline basic sulphate which could not be identified owing to the ferric oxide always contained in it.

The conclusions of Cameron and Robinson are in some important respects opposed to the data of Recoura (*Ann. Chim. Phys.*, 1907, [viii], **9**, 263), as the following table shows :—

Type.	Cameron and Robinson.	Recoura.
Acid...........................	$Fe_2O_3,4SO_3,10H_2O$	$Fe_2O_3,4SO_3,9H_2O$
Normal	$Fe_2O_3,3SO_3,10H_2O$ (one form only)	$Fe_2O_3,3SO_3,9H_2O$ (two isomeric forms)
Basic	None	$6(Fe_2O_3,3SO_3),Fe_2O_3,Aq.$

Thus the evidence of the most careful work on this subject is conflicting in respect of

(1) the hydration of both the acid and the normal salt;

(2) the existence of isomerides of the normal salt; and

(3) the existence of a definite basic compound.

It was partly with a view to clear up some of these discrepancies that a further examination of the solubility relationships of ferric oxide in sulphuric acid solutions was undertaken, the results of which are now presented.

The authors also had in mind the investigation of a product, believed to be a basic sulphate, obtained during the war in the manufacture of "nitrate of iron" mordant from nitre-cake copperas. When ferrous sulphate is oxidised with nitric and sulphuric acids in the manufacture of this mordant, it is found that the introduction of any considerable quantity of sodium sulphate leads to the precipitation of a large proportion of the iron in the form of a finely divided, comparatively insoluble powder, a circumstance which makes the use of nitre-cake for this process impossible either in the original preparation of the ferrous sulphate or as a substitute for sulphuric acid in the oxidation. Repetition of this reaction in laboratory experiments soon showed, however,

that the product was not the expected basic sulphate, but an acid sulphate; the composition determined by analysis was

$$Fe_2O_3,3{\cdot}97SO_3,Aq.$$

As the product appeared to be identical with the acid sulphate investigated by Recoura, it was not considered that further experiments in presence of the sodium salt would contribute anything of value to the investigation. Attention was therefore directed to the repetition and extension of Cameron and Robinson's phase-rule measurements. The chief points in which our measurements differ from those of Cameron and Robinson are

(1) in the investigation of the system, not only at 25°, but also at a lower temperature, 18°;

(2) in a more detailed study of the curves so as to identify the solid phases with more certainty.

Materials.—The water and sulphuric acid used were the ordinary pure materials of the laboratory. During the course of the research two different supplies of ferric sulphate were made use of :—

(*a*) a fine, pale-yellow, microcrystalline ferric sulphate obtained from de Haen as chemically pure, which on analysis showed the presence of only iron, sulphuric acid, and water and corresponded with the formula $Fe_2O_3,3{\cdot}03SO_3,7{\cdot}76H_2O$.

This product was probably the heptahydrate of the normal sulphate containing a little free acid together with absorbed water;

(*b*) a very similar product obtained from Messrs. Griffin, equally free from impurities but containing slightly more free acid. Its composition was $Fe_2O_3,3{\cdot}06SO_3,7{\cdot}55H_2O$.

It is significant that both these salts, reaction products and apparently very pure, contain less than eight but more than seven molecules of water. Attention will be directed to this point again when the phase-rule diagrams shall be under discussion.

The preparation of a suitable ferric oxide or hydroxide for the investigation of the basic side of the curve presented great difficulties. A pure product may be obtained by the ignition of the recrystallised nitrate, but, unfortunately, the ignited oxide becomes very insoluble and requires a very long time to come to equilibrium subsequently in the stirring-bottle. On the other hand, precipitated ferric hydroxide cannot be retained in a crystalline condition if washed free from electrolyte, and in practice, therefore, all methods of washing on filter-paper or by decantation fail when applied to considerable quantities of material. The use of a solution of ferric sulphate itself as wash-water was tried, since the presence of ferric sulphate in the product would have been unobjectionable, but this device proved of no value owing to the fact that ferric oxide is quite considerably soluble in such solutions. Success

was finally attained by the method set forth in the following paragraph, and all the ferric oxide used in this research was prepared in this way.

When a boiling, very concentrated solution of ferric sulphate is precipitated with ammonia, the hydrated oxide, owing to the large concentration of electrolyte present, comes down in coarse, crystalline flakes. These flakes will not remain as such during the necessary washing, since they become colloidal, as already described. But if, before washing, the precipitate is allowed to stand in contact with the liquid from which it was precipitated for eight or ten hours on the water-bath, the crystalline character seems to have more permanence and the precipitate thus treated can be washed with pure water to a state of complete purity. Even so, the reversion to the colloidal condition is only delayed and not entirely prevented and the filtration must be rapid or clogging will take place. Ordinary filter-paper in a funnel or in a Buchner funnel is not sufficiently rapid; the best device has been found to be to filter by means of an evacuated alundnm crucible connected with the pump by means of a rubber bung and immersed in the ferric oxide and washing-water. It was found that nine washings by this method, using for each washing water of about four times the bulk of the precipitate, were sufficient, the water coming from the interior of the filtration crucible being quite free from sulphate.

The Solubility Determinations.

These were performed in mercury-sealed stirring-bottles of the usual type immersed in thermostats, that at 18° being electrically controlled and constant to 0·01° over long periods. The 25° thermostat was gas-regulated and only occasionally showed variations of 0·02°.

The time necessary for the attainment of equilibrium in the stirring-bottles was determined by analysing samples from the same bottle daily until concordant results were obtained. In this way it was found that at 18° the necessary time on the neutral part of the curve was five days. This time too sufficed for the acid part of the curve; the minimum time was not determined, but judging by the appearance of the solutions it was much less than that for the neutral sulphate. Recoura (*loc. cit.*) also states that precipitation of the acid sulphate in a strongly acid solution will be complete in two or three minutes. The mixtures corresponding with the basic part of the curve required longer stirring, a period of seven days elapsing before constant results were obtained.

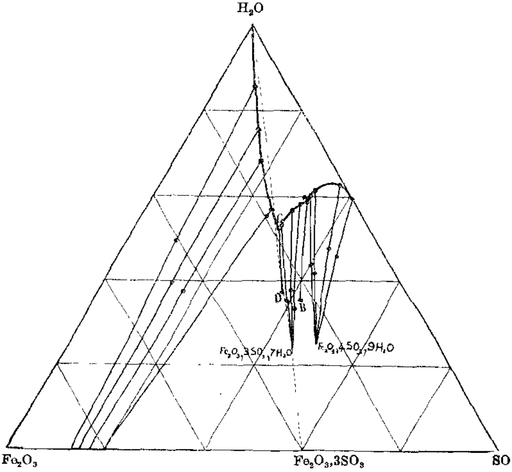
These determinations of the minimum time required for the

establishment of equilibrium do not agree with the experience of Cameron and Robinson, who found that much longer periods of contact, amounting to several weeks, were required at 25° on the basic side. The more favourable conditions of our experiments are probably to be attributed to the use of a ferric oxide prepared in a different manner and having a higher rate of solution than that used by Cameron and Robinson. In all experiments the systems were stirred for longer periods than the minimum, one week being allowed for the neutral and acid regions and ten days or a fortnight for the basic.

Analyses were made in each case of the clear liquid from the stirring-bottle and of the wet solid phase in equilibrium with it. The two points thus obtained on the three-co-ordinate diagram were joined by a tie-line, and the composition of the pure solid phase was obtained by convergence of the tie-lines in the usual Schreinemakers method. The only difficulty which can arise in this method is in the separation of the pure liquid phase from the wet solid, and in this investigation the separation gave no difficulty so long as the liquid phase was acid, that is, so long as the solid phase was the acid or neutral sulphate. When the basic portion of the curves was reached, however, the difficulty of separation became very great. The solid passed through the filter-paper with the liquid; asbestos in a Gooch crucible was no more effective, nor was an alundum crucible. After a considerable amount of experiment, it was found possible to obtain about a gram of the clear liquid by very gentle suction through a very fine alundum crucible. In this way, about the first six drops came through clear; thereafter the solid also came through, but the receiver was removed before this happened. Samples of the wet solid phase were obtained by pouring some of the mixture on a porous plate and scraping off the solid after the liquid had been absorbed. As the curve became more basic, however, even this method broke down, for the porous plate absorbed the solid as well as the liquid. The only method of continuing the investigation was by allowing the phases to separate by long standing in the thermostat and carefully decanting off the clear liquid; this method was not very satisfactory, since the remaining solid was so wet that its composition differed only slightly from that of the liquid, causing considerable uncertainty in the drawing of the tie-lines. Finally, a point was reached at about 25 per cent. SO_3 at which it was impossible to separate the phases even by allowing the solid to settle. At this point the liquid was very viscous and presumably its density was not very different from that of the solid. No separation could be observed after the mixture had been kept for

a fortnight in the thermostat, and three hours' centrifuging was equally ineffective. For this reason there is a gap in the measurements between 25 per cent. and 19 per cent. SO_3. When the concentration of SO_3 fell below 19 per cent., the solutions became less viscous and it was possible to return to the methods which proved successful in the more acid solutions. The points obtained on either side of the gap in the measurements fell on a smooth

Fig. 1.



Temperature 18°.

curve, so that the lack of observations in the interval was of less importance.

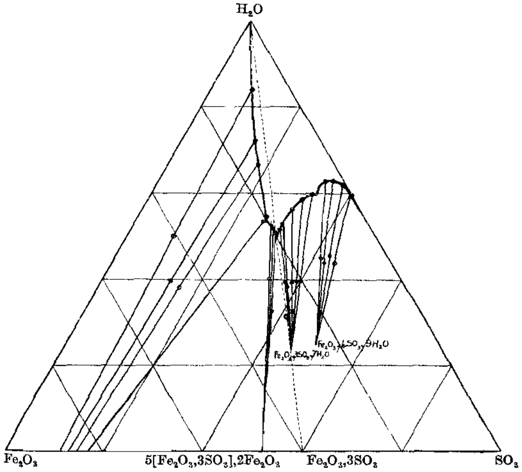
The analytical methods used were the barium chloride method for sulphate, and gravimetric estimation of iron as ferric oxide by precipitation with ammonia, the latter being in many cases supplemented by volumetric estimations with dichromate. Most of the points are the mean of closely concordant analyses of samples taken from the same stirring-bottle after different periods of stirring.

The results are contained in Tables I and II, and are represented graphically in Figs. 1 and 2. The dotted line in each of the figures represents the ratio $Fe_2O_3 : 3SO_3$, that is, that corresponding with the normal salt.

Discussion of Results.

The curve at 25° differs from that at 18° in that it shows three breaks instead of two. Nevertheless, it will be desirable to discuss

Fig. 2.



Temperature 25°.

the two curves together from the point of view of the solid phases concerned.

Acid Sulphate.—When the concentration of SO_3 exceeds 32 per cent. at 18° or 32·2 per cent. at 25°, the solid phase is an acid sulphate. A sample dried on a porous plate proved to be a fine, white, microcrystalline powder, very soluble in water and immediately hydrolysed by it; this is shown by the brown colour of the solutions in water, solutions in acid being colourless. The solubility of this

TABLE I.

Solubilities at 18° (grams per 100 grams).

Liquid Phase.			Wet Solid Phase.			Solid Phase.
Fe_2O_3.	SO_3.	H_2O.	Fe_2O_3	SO_3.	H_2O.	
0·21	40·64	59·15	10·01	44·36	45·63	Acid salt, $Fe_2O_3,4SO_3,9H_2O$.
0·91	36·45	62·64	10·69	41·97	47·34	
6·48	32·43	61·09	16·45	41·93	41·62	
8·00	31·85	60·15	16·01	40·11	43·88	
9·63	31·88	58·49	22·77	41·98	35·25	Acid salt–Normal salt.
11·69	30·80	57·51	25·19	41·36	33·45	Normal salt, $Fe_2O_3,3SO_3,7H_2O$.
13·88	29·71	56·41	23·54	38·80	37·66	
17·48	29·73	52·79	25·66	39·13	35·21	
18·68	29·64	51·68	25·27	37·26	37·47	Normal salt–Basic solid solutions.
17·96	25·42	56·62	19·40	25·43	55·17	Basic solid solutions.
14·00	17·71	68·29	45·45	17·26	37·31	
11·60	13·85	74·55	46·62	14·08	39·30	
6·81	7·60	85·59	40·89	9·61	49·50	

TABLE II.

Solubilities at 25° (grams per 100 grams).

Liquid Phase.			Wet Solid Phase.			Solid Phase.
Fe_2O_3.	SO_3.	H_2O.	Fe_2O_3.	SO_3.	H_2O.	
0·27	39·77	59·96	11·45	44·61	43·94	Acid salt, $Fe_2O_3,4SO_3,9H_2O$.
0·23	40·15	59·62	11·50	44·62	43·88	
0·71	37·22	62·07	11·55	43·10	45·35	
2·38	34·99	62·63	13·47	42·73	43·80	
3·88	33·20	62·92	13·69	41·25	45·06	
8·04	32·06	59·90	20·45	39·78	39·77	Normal salt, $Fe_2O_3,3SO_3,7H_2O$.
10·55	30·77	58·68	21·60	38·96	39·44	
13·80	30·02	56·18	22·62	38·09	39·29	
17·52	29·85	52·63	23·81	37·85	38·34	Basic salt, $5(Fe_2O_3,3SO_3),2Fe_2O_3$.
18·56	29·98	51·46	23·66	36·90	39·44	
19·98	29·19	50·83	30·05	37·19	32·76	Basic solid solutions.
19·79	28·67	51·54	30·87	37·45	31·68	
19·78	27·90	52·32	26·64	33·30	40·06	
19·55	25·99	54·46	20·72	25·60	53·68	
15·53	17·62	66·85	45·77	16·24	37·99	
13·51	14·58	71·91	46·46	13·85	39·69	
7·91	8·19	83·90	40·90	9·13	49·97	

salt decreases rapidly as the concentration of SO_3 increases, and when the SO_3 concentration reaches 38 per cent. at 18° and 40 per cent. at 25° the salt is almost totally insoluble. The liquid phase is quite colourless, and if the acid concentration is increased to about 45 per cent. it is impossible to detect the presence of iron in the solution even with thiocyanate. This remarkable insolubility in strong sulphuric acid possibly explains why the strong acid has no action on metallic iron. It is perhaps suggestive that the lowest strength of acid which can be carried in iron tank-wagons is about 55 per cent. SO_3. The investigation could not be carried to higher acid strengths owing to the increasing insolubility and to the

attack of filtering material by the strongly acid solutions. It was therefore not found possible to obtain any evidence for the existence of Recoura's trihydrate of the acid sulphate from these measurements.

The constitution of the acid salt obtained from the curves agrees very closely at both temperatures with the formula $Fe_2O_3,4SO_3,9H_2O$, which is the formula attributed by Recoura to his ferrisulphuric acid. Cameron and Robinson regard the salt as a decahydrate, but their evidence cannot be regarded as convincing, since they show only two tie-lines intersecting at the composition of the acid salt, and presumably their conclusions are therefore based on two analyses only. It may also be noted that whereas Cameron and Robinson state that the acid–normal eutectic point occurs at an acid concentration of 28 per cent. of SO_3, the present investigation shows that the percentage of SO_3 at this point is much higher (31·88 per cent. at 18° and more than 32 per cent. at 25°). The curves at the two temperatures show that the range of existence of the acid sulphate is more limited at the higher temperature, in accordance with Recoura's observation that the acid salt breaks up into normal salt and free acid on heating.

Normal Sulphate.—Between acid concentrations of 29·64 and 31·88 per cent. of SO_3 at 18° and between about 30 and 32 per cent. of SO_3 at 25° the solid phase in equilibrium with the solutions is the normal ferric sulphate. Samples of this salt dried on a porous plate gave a light brown, microcrystalline powder very soluble in water, although dissolving rather slowly. It will be noted in both diagrams that the curve for the normal sulphate lies wholly to the right of the dotted line. That is, the normal sulphate is not stable in contact with solutions of its own composition, but only in presence of free acid.

The composition of the normal salt comes out very clearly at each temperature as $Fe_2O_3,3SO_3,7H_2O$.

The degree of hydration found for the normal salt is quite opposed to all previous observations. Oudemans (*Rec. trav. chim.*, 1884, **3**, 331), who first prepared the salt in a condition of approximate purity, attributed ten molecules of water to the salt, and the same formula is given by Cameron and Robinson, who, however, do not show the normal salt in their phase-rule curves and do not state the evidence on which their formula is based. Recoura, on the other hand, considers that the salt, like the acid salt, has nine molecules of water. The mineral coquimbite is said to have ten molecules.

Although the indications by the Schreinemakers method are quite clear and definite, the authors have endeavoured to substantiate their conclusions by obtaining a sample of the solid

sufficiently dry to contain less than ten molecules of water. In spite of repeated efforts, success has not been attained, the best result at present being $Fe_2O_3,3{\cdot}2SO_3,11{\cdot}2H_2O$, the point being represented by a cross on the diagram. Although this sample did not contain less than ten molecules of water, it is clearly not the decahydrate moistened with mother-liquor, for its composition is well to the right of the point representing the decahydrate, shown in the 25° diagram by a heavy dot; and it falls exactly on the line cutting the heptahydrate point.

Comparison with the mineral coquimbite was not possible, as a specimen of this mineral was not available, but Mr. T. V. Barker kindly examined the heptahydrate from our equilibrium bottles. The minuteness of the crystals prevented the examination from being very exhaustive, but so far as could be determined the crystallographic properties of the heptahydrate agreed with those of coquimbite.

It would appear from the evidence of the experiments detailed above, which is supported by the composition of the dry solids used as materials in this research, that the normal sulphate is certainly a heptahydrate and that previous data conflicting with this conclusion have been occasioned by the extreme difficulty of freeing the salt from adhering mother-liquor. It is possible that the analyses on which the decahydrate formula for coquimbite is based are subject to a similar error.

The range of existence of the normal salt is somewhat greater at 25° than at 18°. The eutectic points normal–basic and acid–normal were realised at the lower temperature, the former being confirmed by the very obvious separation of the solid in the stirring-bottles into two layers—a lower layer of coarse, light-brown, normal salt and an upper layer of finer material closely resembling ferric oxide in appearance.

Basic Sulphates.—In agreement with Cameron and Robinson's conclusion, it was found that at 25° the greater part of the basic region to the left of the neutral line is occupied by solid phases the composition of which varies continuously with that of the liquid. The same is true of the curve at 18°. Although the investigation of this portion of the curve is extremely difficult owing to the difficulties of separation already referred to, it would appear that the solid phases here are solid solutions of ferric oxide in some basic sulphate the composition of which cannot be obtained from the curve.

There is, however, at 25° some indication of a basic salt, $5[Fe_2O_3,3SO_3],2Fe_2O_3$. Its range of existence is very small. The solid phase on this part of the curve was quite different in appear-

ance from that obtained on the more basic portion of the curve. In the latter case, the solid resembles ferric oxide; in the former, it closely resembles the neutral salt, being, however, somewhat darker in colour. It differed very sharply from the neutral salt in that it could not be separated on filter-paper; the porous plate method had to be used. This basic salt is the only one for which definite phase-rule evidence has yet been obtained. It is remarkable that it contains no water in its constitution.

An attempt was made to determine the formation of a definite basic salt by seeding suitable solutions with a natural basic sulphate, the mineral fibroferrite, $3Fe_2O_3,5SO_3,27H_2O$, but the experiment did not succeed.

As a matter of interest, apart from phase-rule considerations, attempts were made to repeat Recoura's preparation of the substance to which he attributes the basic formula,

$$6[Fe_2O_3,3SO_3],Fe_2O_3,Aq.$$

Pure ferrous sulphate was oxidised with the calculated quantity of nitric acid in presence of the calculated quantity of sulphuric acid. The mixtures of varying concentrations were left to stand in desiccators. One sample was shaken with acetone, as Recoura recommends. In time, varying from twelve days to three weeks, according to the concentration, a solid nucleus formed and the whole mass finally swelled up in the remarkable manner described by Recoura. Some samples of the light-brown, friable mass were pressed out on a porous plate and dried, whilst other samples were first washed with acetone and then dried. Both sets of samples were then analysed, with results in total disagreement with Recoura's statements. Two typical examples are given below :—

Washed in acetone	$Fe_2O_3,3{\cdot}99SO_3,8{\cdot}68H_2O$.
Unwashed	$Fe_2O_3,3{\cdot}92SO_3,8{\cdot}82H_2O$.

These can be nothing else than impure specimens of the acid sulphate. Another fact seems to support this conclusion. If to the viscous solution of ferric sulphate be added one drop of strong sulphuric acid, a white, solid nucleus will at once be formed, and this hastens the swelling and solidification of the solutions very noticeably. Some of the more dilute solutions, in fact, did not solidify at all until encouraged by this seeding with sulphuric acid. Now there can be little doubt that the solid precipitated by strong sulphuric acid is the acid sulphate. It is difficult to conceive why crystals of the acid salt should act as nuclei for the separation of basic salt, unless indeed the acid and basic salts were isomorphous, which is highly improbable.

During the whole course of the investigation only one dry

product was obtained the composition of which was definitely basic. It was observed that alundum crucibles through which ferric sulphate solutions had been filtered, if allowed to stand for ten days to a fortnight, became covered inside and out with a powdery coating which resembled in appearance Recoura's basic sulphate. Samples scraped off and analysed had the composition $10[Fe_2O_3,3SO_3],Fe_2O_3,106H_2O$. It is not likely that a product of such a composition is a pure chemical individual, nor are the means by which it was prepared such as to encourage any belief in its purity. Nevertheless, the contents of some of the bottles were seeded with this powder in the hope that it might have contained a definite basic sulphate. These experiments, however, also gave a negative result.

Summary and Conclusions.

The main results of the present investigation are as follows :—

(1) In contact with solutions of acidity greater than 32 per cent. of SO_3 at 18° or 32·2 per cent. at 25° the stable solid phase is the acid sulphate, $Fe_2O_3,4SO_3,9H_2O$. The range of stability of this salt decreases as the temperature rises.

(2) The solubility of ferric oxide in solutions of acidity greater than 45 per cent. of SO_3 is negligible.

(3) In solutions between 29·6 per cent. and 32 per cent. at 18°, and between 30 per cent. and 32·2 per cent. at 25°, the stable phase is the normal sulphate, which is associated with seven molecules of water, and not nine or ten, as other investigators have reported.

(4) At 25°, between acid concentrations of 27 per cent. to 30 per cent. of SO_3, a solid anhydrous basic salt, $5[Fe_2O_3,3SO_3],2Fe_2O_3$, separates. This compound is not formed at 18°. When the acidity is less than 29·6 per cent. of SO_3 at 18° or 27 per cent. at 25°, the solid phases are solid solutions of variable composition.

No evidence has been found of the existence of other basic sulphates.

(5) The deposits from "nitrate of iron" and the voluminous swollen mass deposited from strong solutions of ferric sulphate on standing are not basic sulphates, but the same acid sulphate as that obtained in acid solutions.

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XLV.—*Optical Activation of Racemic Acid by* l-*Malic Acid.*

By ALEX. MCKENZIE and NELLIE WALKER.

VITH reference to the existence of optically active substances in ıature, van't Hoff predicted the possibility of their formation " bei ınsymmetrischen Versuchsbedingungen, bei Umwandlungen z.B. lie durch die Wirkung des rechts-oder links-cirkularpolarisierten Lichtes stattfinden oder durch aktive Verbindungen veranlasst verden, vielleicht sogar in aktiven Lösungsmitteln " (" Die Lage-ung der Atome im Raume," 2nd edition, 1894, p. 30). Those vords are highly suggestive, and undoubtedly have been the ncentive to much research.

Although asymmetric synthesis in Fischer's interpretation of the erm was not experimentally realised with compounds of known onstitution until 1904, it is more than probable that the idea nay also have occurred independently to van't Hoff when he uses he phrase " durch aktive Verbindungen " in the above quotation. The one-sided manner in which nature builds up substances possess-ng molecular asymmetry has been imitated by Rosenthaler, for example when he synthesised *d*-mandelonitrile from benzaldehyde ınd hydrogen cyanide through the agency of one of the enzymes of emulsin. Whether in this case *d*-mandelonitrile was formed vith the exclusion of the *l*-nitrile is an open question, but on the ıssumption that both nitriles were synthesised to different extents, he preponderance of the *d*-nitrile must certainly have been very great. Again, the recent work of Neuberg on carboligase renders t clear that combination between benzaldehyde and acetaldehyde o form an optically active ketol takes place in a very one-sided nanner. As contrasted with such results achieved by enzyme ıction, the asymmetric syntheses accomplished by the aid of the lirecting influence of compounds of known constitution, for example, -menthol, *l*-borneol, or *d*-amyl alcohol, lead only to a mixture of ınequal amounts of the two enantiomorphous forms. Thus in the ısymmetric synthesis of *l*-atrolactinic acid from benzoylformic ıcid, where the activating agent is *l*-menthol :

$$C_6H_5\cdot CO\cdot CO_2H \text{ (inactive)} \longrightarrow C_6H_5\cdot CO\cdot CO_2\cdot C_{10}H_{19} \text{ (active)} \longrightarrow$$

$$C_6H_5\cdot\underset{OH}{\overset{CH_3}{C}}\cdot CO_2\cdot C_{10}H_{19} \text{ (active)} \longrightarrow C_6H_5\cdot\underset{OH}{\overset{CH_3}{C}}\cdot CO_2H \text{ (active)},$$

he resulting acid had $[\alpha]_D$ $-9{\cdot}5°$ in ethyl-alcoholic solution

(T., 1904, **85**, 1249), whereas the pure *l*-acid has $[\alpha]_D$ $-37{\cdot}7°$ in the same solvent (T., 1910, **97**, 1016). As a matter of fact, in no single case has an asymmetric synthesis been effected with compounds of known constitution where one enantiomorphous form alone has been synthesised.* Still such experiments give the definite proof that only asymmetry can beget asymmetry, and they afford a rational interpretation of the manner in which optical activity can be propagated in nature from one compound to another when once an optically active complex is available at the start. But on the genesis of optical activity in the living plant or animal this ontogenetic method throws no light whatsoever.

Van't Hoff's suggestion of the possibility of a medium like circularly-polarised light exerting a directing influence deals with the bigger problem, and it is interesting to recall that Pasteur himself was also alive to the fundamental importance of this question, for he provided himself with powerful electromagnets for the purpose of testing the influence of a strong magnetic field on an externally-compensated compound (*Revue scientifique*, 1884, [iii], 7, 3). His results were presumably negative, and there is no record of them. Boyd (*Inaug. Diss.*, Heidelberg, 1896) investigated two reactions in each of which a compound containing an asymmetric

* Recently Weiss (*Monatsh.*, 1919, **40**, 391) drew the conclusion that *l*-menthyl *d*-phenyl-*p*-tolylacetate is obtained apart from its diastereoisomeride by the interaction of phenyl-*p*-tolylketen and *l*-menthol:

$$\begin{matrix}C_6H_5\\C_7H_7\end{matrix}\!\!>\!C{:}CO + C_{10}H_{19}{\cdot}OH = \begin{matrix}C_6H_5\\C_7H_7\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}H\\CO_2{\cdot}C_{10}H_{19}\end{matrix}.$$

McKenzie and Miss Widdows (T., 1915, **107**, 702) had previously shown, however, that this ester could not be saponified so as to give the optically pure *d*-acid after the removal of the menthol. Accordingly, when Weiss saponified his ester, he obtained the inactive acid. He is thus in error when he states that he accomplished an asymmetric synthesis, but he has proved the guiding influence of the menthol in its action on the keten, even although the liquid menthyl ester which he obtained may not have been quite homogeneous.

Much confusion would be avoided if the term "asymmetric synthesis" were always used in the restricted sense to which Fischer gave precision (*Ber.*, 1894, **27**, 3231; *Sitzungsber. K. Akad. Wiss. Berlin*, 1902, **28**, 597; *Ber.*, 1903, **36**, 2575. Compare Marckwald, *Ber.*, 1904, **37**, 349; McKenzie, T., 1904, **85**, 1249). In this connexion the misleading statement is made by Jaeger ("Lectures on the Principle of Symmetry," 1917, p. 290) that the first positive results on partial asymmetric synthesis were obtained by Marckwald and McKenzie in the fractional esterification of *r*-mandelic acid by *l*-menthol (*Ber.*, 1899, **32**, 2130). It must be emphasised, however, that the latter authors themselves do not regard this and subsequent work carried out by them on the fractional esterification and hydrolysis of stereoisomerides as examples of asymmetric synthesis at all, since at the very outset a compound is employed which already contains an asymmetric carbon atom.

carbon atom was synthesised in a strong magnetic field. However, neither the stilbene dibromide formed by adding bromine to stilbene nor the mandelic acid prepared by reducing benzoylformic acid with sodium amalgam exhibited any optical activity. According to J. Meyer (*Chem. Ztg.*, 1904, **28**, 41), no positive result could have been expected from Boyd's experiments, since in a homogeneous magnetic field there is a plane of symmetry perpendicular to the lines of force. Meyer accordingly polarised the light before submitting it to the influence of the magnetic field, but his experiments also failed. It may also be mentioned that one of the present authors carried out in 1895 some fruitless experiments on the action of circularly polarised light on aqueous solutions of silver *dl*-lactate and silver *dl*-mandelate. Again, Cotton (*Ann. Chim. Phys.*, 1896, [vii], **8**, 373) investigated the action of circularly polarised light on *dl*-Fehling's solution with negative results, so far as optical activation is concerned, but he made the noteworthy observation that the blue *d*- and *l*-Fehling's solutions possessed different coefficients of optical absorption for circularly polarised light of definite sign. This observation becomes of real importance if Byk (*Z. physikal. Chem.*, 1904, **49**, 641) is correct in his surmise that a constant source of asymmetric circularly polarised light is available on the earth's surface by the reflection of the plane-polarised rays of sunlight from the surface of the sea and the subsequent rotation of those reflected rays by the earth's magnetism. Finally, Henle and Haakh (*Ber.*, 1908, **41**, 4261) deal with the conversion of methylethylcyanoacetic acid into methylethylacetonitrile, and of *s*-dichlorodimethylsuccinic acid into dichlorodimethylpropionic acid. Both reactions were induced by submitting the solutions in the presence of uranium salts to light which was either circularly polarised or was rotated by a magnetic field after having previously been polarised. The results were negative (compare Byk, *Ber.*, 1909, **42**, 141; Freundler, *Ber.*, 1909, **42**, 233).

The third suggestion made by van't Hoff in the lines quoted at the beginning of this paper deals with the possible influence of an optically active solvent as an activating medium, and attempts have been made in various directions to obtain experimental evidence in its favour. Thus Tolloczo (*Z. physikal. Chem.*, 1896, **20**, 412) distributed a racemic compound between two solvents (one of which was optically active) sparingly soluble in one another in order to find out if the compound, when recovered from both solvents, was optically active. *r*-Mandelic acid was distributed between ether and a concentrated aqueous solution of *d*-fructose, but no activity of the mandelic acid regenerated from each of those solvents was observed. Presumably, therefore, *d*-mandelic acid

has the same solubility as its *l*-isomeride in the solution of fructose employed. Similarly, racemic acid was not activated when it was distributed between water and lævorotatory amyl alcohol. Again, after van't Hoff had suggested to Goldschmidt that *d*- and *l*-isomerides might possess different solubilities in an optically active solvent, the solubility of *d*- and *l*-carvoximes in *d*-limonene was measured, when no difference in solubility of the oximes was noted (Goldschmidt and Cooper, *Z. physikal. Chem.*, 1898, **26**, 714). Further, Walden (*Ber.*, 1899, **32**, 1846) examined the displacement of chlorine in *r*-chlorosuccinic acid by the action of potassium hydroxide in the presence of lævorotatory amyl alcohol. The resulting malic acid was optically inactive. Kipping (*P.*, 1900, **16**, 226) prepared benzoin from potassium cyanide and benzaldehyde, a solution of camphor in alcohol being used as the solvent; pyruvic acid was also reduced to lactic acid with aqueous *d*-glucose as the solvent; in each case the products were inactive. Again, E. and O. Wedekind (*Ber.*, 1908, **41**, 456) combined benzylmethylaniline and allyl iodide in an optically active medium such as *l*-menthol or *d*-limonene, but the product in every case was the inactive quaternary iodide.

A positive result was obtained when potassium hydrogen racemate was crystallised from an aqueous solution of *l*-malic acid (T., 1915, **107**, 440). The resulting crystals were dextrorotatory, and consisted of potassium hydrogen racemate with a small admixture of potassium hydrogen *d*-tartrate. The study of this peculiar observation has now been resumed.

Wheu *l*-malic acid was added to an aqueous solution of potassium racemate, the crystals which separated were dextrorotatory, and consisted essentially of potassium hydrogen racemate together with some potassium hydrogen *d*-tartrate (*loc. cit.*). The behaviour of *l*-malic acid towards sodium racemate has now been found to be similar.

Attempts were next made to find out if optical activation could be effected by acids other than *l*-malic acid. No fewer than fifteen other optically active acids were separately tested, and in every case the crystals which were deposited by the addition of the acid to an aqueous solution of potassium or sodium racemate consisted of the acid racemate. Accordingly, of the active acids examined, *l*-malic acid is exceptional in being the only one which caused activation. Racemic acid may possibly also be exceptional, although this point has not been examined in much detail. When *r*-mandelic acid (1 mol.), for example, was neutralised by aqueous sodium hydroxide, and *l*-malic acid (½ mol.) then added, the resulting crystals of sodium hydrogen mandelate exhibited no optical activity.

Similarly, *r*-dimethoxysuccinic acid could not be activated by *l*-malic acid.

The optical rotatory power of the dextrorotatory product from the action of *l*-malic acid on potassium racemate can be enhanced by neutralising with potassium hydroxide and then adding a fresh quantity of *l*-malic acid. After this treatment was repeated several times, the separated crystals were found to possess about double the activity of the initial deposit.

When sodium hydrogen racemate was crystallised from an aqueous solution of *l*-malic acid, it separated from the cold solution in admixture with sodium hydrogen *d*-tartrate. In a similar manner, both rubidium hydrogen racemate and cæsium hydrogen racemate can be activated. On the other hand, when potassium hydrogen racemate was crystallised from an aqueous solution of *l*-mandelic acid, no optical activation was observed, and negative results were also obtained with four other active acids.

So far as the inquiry has gone, there is not sufficient evidence for the conclusion to be drawn that the partial activation of racemic acid by *l*-malic acid is actually due to a resolution of the acid. It is perhaps significant, however, that when an aqueous solution of sodium racemate was mixed with *l*-malic acid and then polarimetrically examined before crystallisation began and after crystallisation ceased, the lævo-value had intensified. If we have to deal with a partial resolution of racemic acid, the case is interesting as providing the first example of the partial resolution of an inactive acid by an active acid instead of by an active base or alcohol. On the other hand, those chemists who are prepared to agree with Erlenmeyer in his recent ingenious claims will find in the present paper several admirable examples of "asymmetric induction."

EXPERIMENTAL.

Addition of l-*Malic Acid to Sodium Racemate.*

An aqueous solution of 10 grams of racemic acid (1 mol.) was neutralised by sodium hydroxide, and 7·97 grams of *l*-malic acid (1 mol.) were added, the solution being made up to 100 c.c. Immediately after the preparation of this solution and before it had started to crystallise, it was polarimetrically examined at the ordinary temperature and found to be lævorotatory, giving $\alpha_D -0·94°$ ($l = 2$). This value remained constant after the solution had been heated on a boiling water-bath for fifteen minutes and the original volume then adjusted when the solution had cooled. The solution was concentrated by evaporation and, on cooling, glassy prisms (6·87 grams) gradually separated, the filtrate (33 c.c.) giving

α_D − 2·41° (l = 2). The solid was dextrorotatory in aqueous solution:

$$l = 2,\ c = 5,\ \alpha_D + 0{\cdot}19°,\ [\alpha]_D + 1{\cdot}9°.$$

The air-dried solid on analysis gave H_2O = 9·5, whereas $C_4H_5O_6Na,H_2O$ requires H_2O = 9·5 per cent. The anhydrous salt gave Na = 13·4; calc. Na = 13·4 per cent.

In another experiment where 5 grams of racemic acid and 4·8 grams of *l*-malic acid were employed, the separated crystals (3·9 grams) were dissolved in water, and the solution (16 c.c.) was examined before crystallisation started, 15 c.c. of it giving + 0·69° in a 2-dcm. tube.

Since the conclusion was drawn from those results and from others which need not be quoted that sodium hydrogen *d*-tartrate crystallises along with its racemic isomeride from solutions prepared in the manner described, it seemed possible that if the original lævorotatory solution obtained by the addition of *l*-malic acid to sodium racemate were allowed to crystallise, polarimetric examination of the liquid in contact with the separated crystals might exhibit an enhanced value in the lævo-direction. Accordingly, an aqueous solution (20 c.c.) of sodium racemate prepared by the neutralisation of 2 grams of racemic acid was quickly mixed with an aqueous solution (20 c.c.) of 1·6 grams of *l*-malic acid, and the resulting solution then polarimetrically examined; the value α_D − 0·47° (l = 2) was noted. As crystallisation had started only slightly, the solution was evaporated to smaller bulk, and part of it examined before crystallisation started, giving α_D − 0·90° (l = 2). On remaining over-night in the polarimeter tube, glassy crystals had separated, but the supernatant liquid was clear, so that polarimetric readings of it could be taken with ease; the lævorotation had perceptibly increased to α_D − 1·20°. After an additional three days this value had increased to α_D − 1·37°, which latter value was again observed a day later.

Activation of Alkali Hydrogen Racemates by Crystallisation from an Aqueous Solution of l-*Malic Acid.*

Sodium Hydrogen Racemate.—8·1 Grams of this salt were added to 32 c.c. of an aqueous solution containing 5·71 grams of *l*-malic acid. After heating on the water-bath for half an hour, the clear solution was cooled, and crystallisation started. The crystals were drained and washed with 10 c.c. of water. The air-dried product amounted to 6 grams, and the analysis conducted with a portion dried at 120—130° gave Na = 13·2 (calc. 13·4) per cent. It was *dextrorotatory*; 2·5 grams of it were neutralised with sodium

hydroxide and the whole of the solution was examined in a 2-dcm. tube, when the value $\alpha_D + 0{\cdot}37°$ was observed. The numerical value of this dextrorotation was increased by the addition of boric acid. 1·57 Grams of the crystals were mixed with 1·5 grams of boric acid, and the aqueous solution of the mixture gave $\alpha_D + 0{\cdot}77°$ $(l = 2)$.

Rubidium Hydrogen Racemate.—This salt was prepared by neutralising racemic acid with rubidium hydroxide and then adding the calculated amount of *N*-sulphuric acid to the hot solution; crystallisation of the acid salt started quickly on cooling. Rubidium hydrogen racemate (9·8 grams) was dissolved by boiling with 130 c.c. of an aqueous solution containing 5·6 grams of *l*-malic acid. The crystals which separated from the cold solution amounted to 7·9 grams, and an analysis of the air-dried salt gave Rb = 36·6 ($C_4H_5O_6Rb$ requires Rb = 36·4 per cent.). The aqueous solution prepared by neutralising 4 grams of this salt with rubidium carbonate gave $\alpha_D + 0{\cdot}34°$ when examined in a 2-dcm. tube.

In order to make certain that the activity noticed was actually caused by the agency of malic acid, rubidium hydrogen racemate was crystallised from boiling water, and the optical inactivity of the crystals which separated determined.

Cæsium Hydrogen Racemate.—Ten grams of this salt were heated with 100 c.c. of an aqueous solution containing 4·6 grams of *l*-malic acid. 4·8 Grams separated (Found: Cs = 47·1; calc., Cs = 47·1 per cent.). 3·5 Grams were added to water and neutralised by cæsium carbonate; when polarimetrically examined, the solution gave a distinct shadow in the dextro-direction, the value noted being $\alpha_D + 0{\cdot}11°$ $(l = 2)$.

No optical activation of racemic acid was observed to have taken place when the following optically active acids were substituted for *l*-malic acid: *l*-lactic acid, *l*-mandelic acid, *l*-acetylmandelic acid, *d*-ethoxysuccinic acid, *d*-dimethoxysuccinic acid, *d*-dimethoxysuccinamic acid, *l*-phenylmethoxyacetic acid, *l*-tropic acid, *l*-β-hydroxy-β-phenylpropionic acid, *d*-β-hydroxy-β-phenylpropionic acid, *l*-quinic acid, *d*-camphoric acid, *l*-camphanic acid, *l*-asparagine, *l*-aspartic acid. The procedure was on the lines which gave positive results with *l*-malic acid, the active acid in each case being added to the aqueous solution of potassium or sodium racemate. The resulting crystals exhibited no distinct optical activity when examined in alkaline solution. Moreover, when potassium hydrogen racemate was dissolved in an aqueous solution of *l*-mandelic acid, the crystals which separated were optically inactive when examined in the usual way. A similar result was obtained when aqueous

solutions of *d*-camphoric acid, *l*-aspartic acid, *d*-β-hydroxy-β-phenylpropionic acid, and *d*-dimethoxysuccinic acid were respectively employed as the solvent for the potassium hydrogen racemate.

Mandelic acid has the property of forming acid salts, for example, barium hydrogen *r*-mandelate (T., 1899, **75**, 969). Potassium hydrogen *r*-mandelate can be easily prepared by neutralising mandelic acid by potassium hydroxide and adding to the aqueous solution an amount of mandelic acid equal to that neutralised. The acid salt separates from water in glassy prisms, and mandelic acid is obtained from its aqueous solution by extraction with ether. The acid sodium salt, prepared in a similar manner, separates from water in prisms grouped in rosettes. Mandelic acid, unlike racemic acid, undergoes no optical activation whatsoever when examined in its behaviour towards *l*-malic acid. The salt obtained by adding *l*-malic acid (½ mol.) to the solution of sodium mandelate prepared from mandelic acid (1 mol.) was found to be optically inactive in aqueous solution, and it gave *r*-mandelic acid on extraction with ether. Analysis of this salt gave Na = 6·9.

$$OH{\cdot}CHPh{\cdot}CO_2H,OH{\cdot}CHPh{\cdot}CO_2Na$$

requires Na = 7·0 per cent.

Neither acid sodium mandelate nor acid potassium mandelate is activated by crystallisation from an aqueous solution of *l*-malic acid. The acid sodium mandelate obtained by the addition of the requisite quantity of *d*-tartaric acid to an aqueous solution of sodium *r*-mandelate was also devoid of optical activity.

Finally, in place of racemic acid, *r*-dimethoxysuccinic acid was taken. Barium *r*-dimethoxysuccinate (12 grams) was converted into the potassium salt, to the aqueous solution of which *l*-malic acid (4 grams) was added. 3·6 Grams of potassium hydrogen *r*-dimethoxysuccinate were isolated, and when this was neutralised no optical activity at all could be detected.

Addition of l-*Malic Acid to Potassium Racemate.*

16·8 Grams of racemic acid (1 mol.) were neutralised by aqueous potassium hydroxide, and the solution was made up to 840 c.c. To the warm solution *l*-malic acid (13·4 grams, 1 mol.) was added, and crystals soon began to separate from the clear solution. The crystals (17·7 grams) were neutralised by potassium hydroxide, and the solution (177 c.c.) was examined in a 2-dcm. tube containing about 15 c.c. The value α_D + 0·30° was observed. The potassium salt contained in this solution corresponded with 15·8 grams of racemic acid, and the solution after dilution was accordingly treated with 12·6 grams of *l*-malic acid (1 mol.). The resulting crystals were again neutralised, and after polarimetric examination of a

portion of the solution the whole of the latter was treated with a fresh quantity of malic acid. This process was repeated several times, with the results tabulated below. The volume relationships were comparable throughout; in the crystallisation of the sparingly soluble acid salts the concentration corresponded with 1 gram of racemic acid (hydrated) in 50 c.c. of solution, whilst for the polarimetric estimation the acid salts were neutralised by potassium hydroxide and the volume adjusted so that 1 gram of acid salt was contained in 10 c.c. of the neutral solution. The crystals in each case were weighed after having been dried at 100° for one hour.

In the following table, A = equivalent weight of racemic acid (hydrated), calculated from the weight of crystals; B = weight of malic acid (1 mol.); C = total volume; D = weight of crystals; E = rotation of crystals after neutralisation by potassium hydroxide, $c = 10$.

A.	B.	C.	D.	E.
15·8 grams	12·6 grams	790 c.c.	14·7 grams	α_D + 0·37°
13·13 ,,	10·47 ,,	656 ,,	12·52 ,,	0·54
11·18 ,,	8·92 ,,	559 ,,	9·96 ,,	0·62
8·9 ,,	7·1 ,,	445 ,,	7·62 ,,	0·68
6·81 ,,	5·43 ,,	340 ,,	5·97 ,,	0·66
5·34 ,,	4·26 ,,	267 ,,	4·68 ,,	0·60
4·18 ,,	3·34 ,,	209 ,,	3·41 ,,	0·60

The solution (34·1 c.c.) containing the final product (3·41 grams) was evaporated and the whole of it examined in a 2-dcm. tube, when the value α_D + 1·35° was observed. This dextrorotation was intensified by the addition of boric acid to the solution.

We desire to express our thanks to the Carnegie Trust for the assistance afforded in the prosecution of this research. We are also indebted to Principal Irvine for placing at our disposal specimens of zinc ammonium *d*-lactate and barium *r*-dimethoxysuccinate, and to Dr. C. R. Young, who provided us with *d*-dimethoxysuccinamic acid.

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University of St. Andrews. [*Received, January 11th*, 1922.]

XLVI.—*A Rapid Iodometric Estimation of Copper and Iron in Mixtures of their Salts.*

By Ian William Wark.

The iodometric method of analysis has long been used in the estimation of copper, and the conditions under which the best results are obtained are now well known. Although an analogous method is available for iron, little use has been made of it, owing to the number of good methods already worked out and partly, no doubt, to the high cost of potassium iodide.

This method of estimation of either metal must therefore fail in the presence of the other. Moser (*Z. anal. Chem.*, 1904, **43**, 597) has put forward a method by which copper can be estimated in the presence of iron salts. By the addition of sodium pyrophosphate to either cupric or ferric salts, precipitates are at first formed; these dissolve in excess of the phosphate. In the presence of acetic acid, both the soluble complex and the insoluble phosphate liberate iodine from potassium iodide in the case of copper, but not in that of iron. So if phosphate be added to a mixture of copper and iron salts, and then an iodometric titration performed, the result will correspond with the copper present only.

Ley (*Chem. Ztg.*, 1917, **47**, 763) has proposed an extension of this process, by which iron can also be estimated. Copper is first estimated by Moser's method. The original solution is then titrated without addition of phosphate, when the iodine liberated corresponds with the sum of copper and iron. Iron is then calculated by difference. Ley seems to have been ignorant of the excellent work of Moser, and it is difficult to judge the accuracy of the method from his paper.

The method proposed by the present author takes advantage of the fact that although ferric phosphate in the presence of acetic acid does not liberate iodine from potassium iodide, it does so in the presence of mineral acids. Copper is estimated iodometrically, after addition of phosphate, by Moser's method. Mineral acid is now added to the titrated solution, when a second liberation of iodine, corresponding with the iron present, occurs.

It is obvious that the method effects a great saving in time and materials in comparison with Ley's method, rendering it suitable to estimations which are required quickly. It is very accurate where the metals are present in approximately equal amounts, and gives fair results over a wide range. Furthermore, iron is directly estimated.

EXPERIMENTAL.

A. *Estimation of Iron Iodometrically.*—It was thought advisable to carry out a preliminary series of experiments on this estimation. The results showed that if the following conditions are observed, good results can be obtained.

(1) The solutions should be moderately concentrated.

(2) An excess of potassium iodide over that required by the equation $FeCl_3 + KI = FeCl_2 + KCl + I$ is necessary. Three grams suffice for 0·1 gram of iron.

(3) In order to increase the velocity of the reaction, a few c.c. of dilute mineral acid should be added. A large amount of acetic acid should be avoided, since this would lower the result slightly.

(4) It is advisable to commence the titration five minutes after adding the potassium iodide, and to work in a stoppered flask, which should be well shaken before the end-point is reached.

(5) With dilute solutions, it is advisable to double the amount of potassium iodide, and to raise the temperature to 50° after the end-point is reached. A small amount of iodine may then be liberated by hitherto unreduced iron. This should never correspond with more than about 1 per cent. of the total iron. $N/100$-Solution can be used if these precautions are observed.

As ferrous iodide is not precipitated, the end-point is observed much more easily than in the case of copper. It is quite easy to detect it even when the solutions are $N/100$. No indicator is required.

Table I will give an idea of the degree of accuracy of the method, and illustrate the kind of evidence on which the above suggestions are based. Further figures can be seen in a recent paper by Kolthoff (*Pharm. Weekblad,* 1921, **58**, 1510), where the author claims that it is better to work with chlorides than with sulphates. It would appear, however, from the present work that, if sufficient potassium iodide be added, it is quite safe to work even with sulphates. Some results on the velocity of the reaction in neutral solution have been published by Seubert and others (*Z. anorg. Chem.*, 1894–1895), but no attempt was made to apply the process to the estimation of iron.

The solutions here employed were $N/10$-ferric sulphate and $N/10$-sodium thiosulphate. The former was standardised gravimetrically after precipitation with ammonia; the latter against pure copper (Low's method). Where the above recommendations have been followed, the error is always within 5 parts per 1000.

Ten c.c. of iron solution were used throughout.

TABLE I.

Grams of KI added.	C.c. of 6*N*-H_2SO_4.	C.c. of 80% acetic acid.	Time of keeping. Minutes.	C.c. of $Na_2S_2O_3$ (Theor. = 10 c.c.).	Error per cent.
0·5	—	—	5	9·0	10
1	—	—	,,	9·82	1·8
1	—	—	30	9·95	0·5
2	—	—	5	9·95	0·5
3	—	—	,,	10·00	—
,,	1	—	,,	10·00	—
,,	5	—	,,	9·98	0·2
,,	—	1	,,	9·98	0·2
,,	—	5	,,	9·92	0·8
,,	—	10	,,	9·82	1·8
1·5	2	—	,,	9·95	0·5
1	5	—	,,	10·02	0·2
2	5	10	15	9·98	0·2

B. *Effect of Phosphate on the Copper Estimation.*—Experiments were now carried out which showed that the addition of disodium phosphate to a copper solution containing free acid was without influence on the end-point. If more than 2 grams of phosphate be added per 0·1 gram of copper, it is necessary to add a considerable amount of acetic acid in order to get a theoretical yield of iodine. The temperature, the amount of mineral or acetic acid, and the nature of the precipitating phosphate are without influence on the end-point.

C. *Effect of Phosphate on the Iron Estimation.*—If about three times the theoretical amount of phosphate which would be necessary completely to precipitate the iron as ferric phosphate be added, no iodine is liberated even in acetic acid solution. At 80° the liberation has not begun. Free mineral acid does, however, liberate iodine even when a large excess of phosphate is present, and if sufficient acid be added, a theoretical yield of iodine will be obtained. It is advisable to set the mixture aside for a few minutes before titrating.

D. *Estimation of Copper in the Presence of Iron.*—Moser has shown that copper can be fairly accurately estimated in the presence of iron by his method outlined above. His results have been confirmed, and the following conditions are put forward as satisfactory.

(1) The solution must not contain free mineral acid. If it be acid originally, the free acid is best neutralised with ammonia, as moderate amounts of ammonium salts do not seriously affect the end-point. If iron be present in the ferrous state, boiling with a few drops of bromine and sulphuric acid will readily convert it into the ferric state. It is, of course, necessary completely to expel the excess of bromine by boiling.

(2) The solution should be as concentrated as possible.

(3) Three grams of potassium iodide and 5 c.c. of acetic acid should be added for each 0·1 gram of total metal present, and 2 grams of disodium phosphate for each 0·1 gram of iron.

(4) The mixture should be kept for five or ten minutes before titrating.

(5) For mixtures low in copper (less than 5 per cent.) double this amount of phosphate should be added. After titration to the end-point the mixture should be warmed at 50°, kept for another five minutes, and, if necessary, more thiosulphate added.

Some idea of the accuracy of this method can be gained from Table II (ignoring the last two columns). If these conditions be fulfilled, the error should not exceed 0·5 per cent. of the total copper, and will usually be less. An attempt has been made to extend the method over a wider range than that investigated in Moser's work, but it is here pointed out that the accuracy of the method necessarily falls off as the ratio of the weights of the two metals increasingly differs from unity.

E. *Estimation of both Copper and Iron in Mixtures.*—In this section the method proposed by the author is discussed. Copper is first determined as in D. Then to the titrated mixture sulphuric acid is added, when a second liberation of iodine corresponding with the iron occurs. Thus a second titration against thiosulphate gives the iron content.

In addition to the recommendations already made under D, the following are added.

(1) Ten c.c. of $6N$-sulphuric acid should be added per 0·1 gram of metal.

(2) The mixture should be kept for five or ten minutes before titrating.

Table II illustrates the type of results which are obtained by the methods of this and the preceding section. The copper sulphate solutions were standardised electrolytically. In those experiments (2, 4, 6, 8, 10, 12, 15, 16) where the above instructions have been fairly closely followed, the error is almost always less than 0·5 per cent. of the metal present, and often smaller than that.

The method becomes more troublesome with such low percentages of copper as in 11 and 12 (1·5 per cent.). In order to get the theoretical value for copper, a large excess of phospbate must be added. On addition of sulphuric acid, this retards the liberation of iodine. (See D 5 above.) For such cases, it may be expedient to use Ley's method. The method remains good with low percentages of iron, but from its nature is unsuitable for very low iron content; a separation seems impossible in these cases.

It is not claimed that the method is exceedingly accurate over

TABLE II.

Expt.	C.c. of $Fe_2(SO_4)_3$ taken.		C.c. of $CuSO_4$ taken.		Grams of KI added.	Grams of $Na_2HPO_4,12H_2O$ added.	C.c. of acetic acid (80%) added.	First titration. C.c. of $Na_2S_2O_3$. Measured.		First titration. Calc.	C.c. of H_2SO_4 added after the first titration.	Second titration. C.c. of $Na_2S_2O_3$. Measured.		Second titration. Calc.
	N/10.	*N*/100.	*N*/10.	*N*/100.				*N*/10.	*N*/100.			*N*/10.	*N*/100.	
1	10		10		4	1	2	10·15		10	5	9·82		10
2	,,		,,		,,	2	5	9·98		,,	,,	10·05		,,
3		10		10	2	0·5	2		9·85	,,	2		10·18	,,
4		,,		,,	,,	0·2	5		9·82	,,	,,		10·25	,,
5	5		10		4	1	2	9·92		,,	,,	5·00		5
6	,,		,,		3	,,	5	9·95		,,	5	5·02		,,
7	10		5		,,	2	2	4·92		5	,,	9·98		10
8	,,		,,		2	,,	5	5·02		,,	,,	10·02		,,
9	,,			10	3	1	2		9·78	10	,,	9·80		,,
10	,,			,,	,,	,,	5		9·88	,,	10	9·92		,,
11	20			3	2	,,	2		7·0	3				
12	,,			,,	3	5	5		2·75	,,	,,	19·95		20
13		10	10		,,	1	2	9·90		10	2		10·40	10
14		,,	,,		,,	0·5	5	10·05		,,	,,		10·15	,,
15		,,	,,		2	1	5	9·98		,,	5		10·30	,,
16		3	20		3	0·5	2	19·95		20	,,		3·20	3

a very wide range. It is, however, a rapid method, capable of giving results quite good enough for most purposes, and should be useful particularly where apparatus for electrolysis is not available.

Summary.

(1) The iodometric estimation of iron has been investigated and certain recommendations have been put forward concerning its application.

(2) The effect of phosphate on the iodometric estimation of (*a*) copper, (*b*) iron has been studied.

(3) A method for the estimation of copper in the presence of iron has been examined.

(4) An extension of this method has been put forward by which both copper and iron can be estimated in the same solntion.

The preliminary part of this work was carried out at Melbourne University, and the author wishes to express his thanks to Professor Masson, who, by assistance in many ways, rendered the work possible.

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XLVII.—*The Combustion of Complex Gaseous Mixtures.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

WITH each of the paraffin hydrocarbons the speed of the uniform movement of flame in its limit mixtures with air is approximately the same under standard conditions of experiment. Thus the speeds as determined in a horizontal glass tube 2·5 cm. in diameter are :

	Speed of uniform movement of flame. Cm. per sec.	
	Lower limit mixture.	Upper limit mixture.
Methane	23·3	19·1
Ethane	18·1	19·7
Propane	20·8	20·3
Butane	20·1	20·3
Pentane	20·2	20·2

Under the same conditions of experiment, approximately the

same speed of uniform movement of flame is obtained with all limit mixtures of methane, oxygen, and nitrogen, and, for example, with an equimolecular mixture of methane and pentane at its limits with air:

Mixture.	Speed of uniform movement of flame in a horizontal glass tube 2·5 cm. in diameter. Cm. per sec. Lower limit mixture.	Upper limit mixture.
Methane with atmosphere containing 13·7 per cent. of oxygen	21·9	19·1
Methane with atmosphere containing 17·0 per cent. of oxygen	22·4	19·0
Methane with air	23·3	19·1
Methane with atmosphere containing 33·0 per cent. of oxygen	23·0	18·9
Methane with atmosphere containing 50·0 per cent. of oxygen	22·8	18·9
Methane with atmosphere containing 66·0 per cent. of oxygen	21·3	19·4
Methane with oxygen	19·9	18·9
Equimolecular mixture of methane and pentane with air	22·3	20·7

In general, if a limit mixture with air of one gas is mixed, in any proportions, with a limit mixture with air of another gas, the speed of propagation of flame in both mixtures being, as it is, approximately the same under the same conditions of experiment, the speed of propagation of flame in the resultant complex mixture (which is also a limit mixture) is unchanged.*

This law, which can be termed the law of speeds of flame in complex gaseous mixtures, can be shown experimentally to hold, with considerable accuracy, for the propagation of flame, not only in limit mixtures, but in all mixtures of inflammable gases with air (or oxygen), provided that the mixtures of the individual gases are of the same type, all containing excess of oxygen or all containing excess of combustible gas. For example, a mixture of methane and air containing 7·35 per cent. of methane, and a mixture of pentane and air containing 1·98 per cent. of pentane, were prepared. In these two mixtures the speed of the uniform movement of flame under the same conditions of experiment is the same, about 40 cm. per sec. in a horizontal glass tube 2·5 cm. in diameter, and they both contain excess of oxygen. The mixtures were combined in varying proportions and the speeds of the uniform movement of flame in the resultant complex mixtures then determined, as follows:

* Provided that the limit mixtures of the individual gases are of the same [illegible] [illegible]th lower or both upper.

Speeds of uniform movement of flame in a horizontal glass tube 2·5 cm. in diameter with mixtures containing 7·35 per cent. of methane and 1·98 per cent. of pentane, respectively, mixed together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed of flame. Cm. per sec.
100·0	nil.	39·3
75·0	25·0	39·2
50·0	50·0	39·6
25·0	75·0	39·9
21·2	78·8	39·2 *
nil.	100·0	40·1

* *Methane and pentane in equimolecular proportions.*

It will be seen that the speeds are identical within the limits of experimental error.

Similarly, two mixtures containing excess of combustible gas were examined in the same manner. These mixtures contained 11·00 per cent. of methane and 3·54 per cent. of pentane, respectively, and the speed of the uniform movement of flame in them was about 60 cm. per sec. in a horizontal glass tube 2·5 cm. in diameter.

Speeds of uniform movement of flame in a horizontal glass tube 2·5 cm. in diameter with mixtures containing 11·00 per cent. of methane and 3·54 per cent. of pentane, respectively, mixed together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed of flame. Cm. per sec.
100·0	nil.	59·1
75·0	25·0	59·1
50·0	50·0	60·3
25·0	75·0	59·1
24·4	75·6	59·1 *
nil.	100·0	59·6

* Methane and pentane in equimolecular proportions.

Further examples of the experimental verification of this "law of speeds" with a number of different inflammable gases in admixture with air or oxygen are given in T., 1919, **115**, 1446, 1454; 1920, **117**, 48. It can be stated as follows: Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures of the same type * propagate flame at the same speeds, under the same conditions of experiment.

It follows that, so far as the propagation of flame is concerned, a mixture of a number of different combustible gases with air

* All containing excess of oxygen or all containing excess of combustible gas.

(for example) can be regarded as the summation of mixtures of each individual gas with air, the proportions of combustible gas and air in each being such that the speed of flame in it, if the mixture were burning alone, would be the same as in the complex mixture.

For example, a mixture of air, methane, and hydrogen containing 9·00 per cent. of the equimolecular mixture $CH_4 + H_2$ (or 4·5 per cent. of each inflammable gas) propagates flame, under given experimental conditions, at a speed of 45 cm. per second. Under the same experimental conditions, a speed of flame of 45 cm. per second is obtained with 7·65 per cent. of methane alone in air. In this simple mixture, the 7·65 per cent. of methane is associated with (100 − 7·65) per cent. of air. According to the "law of speeds," therefore, the 4·5 per cent. of methane in the complex methane–hydrogen–air mixture postulated is associated with $\frac{4·50}{7·65}$ (100 − 7·65) per cent. of air. Similarly, under the same experimental conditions, a speed of flame of 45 cm. per second is obtained with 10·90 per cent. of hydrogen alone in air. In this simple mixture, the 10·90 per cent. of hydrogen is associated with (100 − 10·90) per cent. of air; therefore in the complex methane–hydrogen–air mixture the 4·5 per cent. of hydrogen is associated with $\frac{4·50}{10·90}$ (100 − 10·90) per cent. of air. The ratio between (*a*) the air associated with, or monopolised by, the methane, and (*b*) the air monopolised by the hydrogen, during the propagation of flame in the complex methane–hydrogen–air mixture, is thus:

$$\frac{100 - 7·65}{7·65} : \frac{100 - 10·90}{10·90} = 12·1 : 8·2.$$

In the mixture chosen for this example there is sufficient oxygen present in the air to burn all the methane and hydrogen completely. Let us consider one in which the oxygen is in defect. A mixture of air with 18·80 per cent. of the equimolecular mixture $CH_4 + H_2$ (9·4 per cent. of each inflammable gas) propagates flame under given experimental conditions at a speed of 60 cm. per second. Under the same conditions, that speed of flame is obtained with either 10·85 per cent. of methane alone in air or 71·00 per cent. of hydrogen alone in air. In these simple mixtures the methane is associated with (100 − 10·85) per cent. of air and the hydrogen with (100 − 71·00) per cent. of air. In the complex methane–hydrogen–air mixture, therefore, the 9·4 per cent. of methane is associated with $\frac{9·4}{10·85}$ (100 − 10·85) and the 9·4 per

cent. of hydrogen with $\frac{9 \cdot 4}{71 \cdot 0}$ (100 — 71·0) per cent. of air; so that the ratio between the air monopolised by methane to that monopolised by hydrogen during the propagation of flame in the complex *mixture is :*

$$\frac{100 - 10 \cdot 85}{10 \cdot 85} : \frac{100 - 71 \cdot 0}{71 \cdot 0} = 8 \cdot 2 : 0 \cdot 4.$$

Since in this mixture there is insufficient oxygen to burn the whole of both the methane and the hydrogen, it must be presumed that the relative proportions of oxygen that will combine with the methane and the hydrogen respectively will be determined by the relative amounts of air "monopolised" by each during the propagation of flame at the given speed.

In general, it can be concluded that during the propagation of flame in a mixture of several inflammable gases with air at a given speed, the gas which will monopolise the most oxygen is that *which when burning alone with the same speed of flame is associated* with the most air.

These are natural deductions to draw from the law of speeds. They have been tested experimentally, in a manner now to be described.

Suppose that flame is allowed to travel through a mixture of methane, hydrogen, and air, the oxygen present being insufficient for the complete combustion of both gases. If the deductions drawn from the law of speeds (which holds remarkably closely for mixtures of methane, hydrogen, and air) are correct, then the *products of combustion of the complex mixture should have the* same composition as when a methane–air mixture and a hydrogen–air mixture are inflamed separately and the products of combustion of each are mixed together, provided that the speed of propagation of flame in the two separate mixtures is the same as in the complex mixture.

The determination of the distribution of oxygen between different inflammable gases such as methane and hydrogen is complicated by the occurrence of the secondary "water-gas reaction," which modifies the composition of the final products of combustion. An *increase or decrease in the volume of carbon monoxide found in* the final gases, above or below that formed before the water-gas reaction came into play, is, however, accompanied by a corresponding decrease or increase in the volumes of carbon dioxide and hydrogen found, according to the equilibrium $CO_2 + H_2 \rightleftharpoons CO + H_2O$, and calculation can be made of the amount of change.

Three series of experiments can be recorded, as follow.

TABLE I.—*Upper Limit Mixtures with Oxygen.*

Inflammable gas :—		Methane.		Hydrogen.		Carbon monoxide.	
Analysis of limit mixture. Per cent.		O_2	42·88	O_2	7·69	O_2	6·32
		CH_4	57·12	H_2	92·31	CO	93·68
Experiment No.		1*a*	1*b*	2*a*	2*b*	3*a*	3*b*
Analysis of products of combustion (calculated nitrogen-free). Per cent.	CO_2	3·18	3·17	—	—	13·43	13·40
	CO	36·17	36·17	—	—	85·72	85·74
	CH_4	3·25	3·25	—	—		
	H_2	57·40	57·41	100·00	100·00	0·85	0·86
Ratio p_2/p_1		1·34	1·34	0·769	0·769	0·945	0·945
Partial pressures of individual constituents of products of combustion. Atmospheres.	CO_2	0·0425	0·0424			0·1269	0·1266
	CO	0·4846	0·4846			0·8100	0·8102
	CH_4	0·0435	0·0435				
	H_2	0·7691	0·7692	0·7690	0·7690	0·0080	0·0081

TABLE II.

Inflammable gases :—		$CH_4 + H_2$		$H_2 + CO$		$CO + CH_4$	
Analysis of mixture. Per cent.		O_2	29·74	O_2	7·14	O_2	30·77
		CH_4	35·23	H_2	47·04	CO	35·18
		H_2	35·03	CO	45·82	CH_4	34·05
Experiment No.		4*a*	4*b*	5*a*	5*b*	6*a*	6*b*
Analysis of products of combustion (calculated nitrogen-free). Per cent.	CO_2	2·33	2·30	4·19	4·15	6·71	6·73
	CO	26·38	26·32	51·79	51·92	52·06	52·15
	CH_4	3·38	3·42	—	—	2·72	2·76
	H_2	67·91	67·96	44·02	43·93	38·51	38·36
Ratio p_2/p_1		1·10	1·10	0·819	0·819	1·13	1·13
Partial pressures of individual constituents of products of combustion. Atmospheres.	CO_2	0·0256	0·0254	0·0343	0·0340	0·0758	0·0760
	CO	0·2901	0·2895	0·4247	0·4253	0·5881	0·5893
	CH_4	0·0372	0·0377	—	—	0·0307	0·0312
	H_2	0·7470	0·7475	0·3610	0·3597	0·4351	0·4355

I.—*Upper Limit Mixtures with Oxygen.*

The combustible gases used were methane, hydrogen, and carbon monoxide. The limits were determined, within about 0·5 per cent., for downward propagation of flame in a glass tube 2 cm. in diameter and 40 cm. long, closed at both ends. Each limit mixture was ignited at atmospheric pressure; the pressure of the cooled products of combustion was then determined and analysis made of them, whence the partial pressure of each product could be calculated. The results of duplicate experiments are recorded in Table I.

From these results it should be possible, if our deductions from the "law of speeds" are correct, to calculate what would be the composition of the products of combustion of any mixture of these upper-limit mixtures, for the speed of flame is the same in each. The mixtures were therefore blended, two at a time, the blend chosen in each instance being that which contained approximately equimolecular proportions of the two inflammable gases. These complex mixtures (which were, like the simple mixtures, upper-limit mixtures) were then ignited and their products of combustion measured and analysed. The results are recorded in Table II, whilst in Table III comparison is made between the values for the products of combustion obtained experimentally and those calculated from Table I. In none of the experiments was carbon deposited, nor did more than a trace of oxygen remain unburnt.

It will be seen that there is close correspondence between the "calculated" and "observed" values for the individual products of combustion.

II.—*Upper Limit Mixtures of Methane, Oxygen, and Nitrogen.*

The "law of speeds" holds, not only with respect to different inflammable gases mixed with oxygen or with the same "atmosphere" of oxygen and nitrogen, but also with respect to the same inflammable gas mixed with different "atmospheres." Experiments were therefore made to determine whether the composition of the products of combustion of any mixture of methane, oxygen, and nitrogen can be calculated, given the composition of the products of combustion of two other mixtures in which the proportions of methane, oxygen, and nitrogen are different but in which the speed of flame is the same.

The mixtures chosen to supply the experimental data from which to make calculations were the upper-limit mixtures (downward propagation of flame) of methane with (1) air and (2) oxygen.

TABLE III.*

Experiment No.		Partial pressures of products of combustion. Calculated.			Partial pressures. Found.		
4		From Expt. 1*a*. 35·23 per cent. CH_4 yields :	From Expt. 2*a*. 35·03 per cent. H_2 yields :	Total.	4*a*.	4*b*.	Mean.
	CO_2	2·62	—	2·62	2·56	2·54	2·55
	CO	29·90	—	29·90	29·01	28·95	28·98
	H_2	47·45	26·95	74·40	74·47	74·75	74·61
	CH_4	2·68	—	2·68	3·72	3·77	3·74
5		From Expt. 2*a*. 47·04 per cent. H_2 yields :	From Expt. 3*a*. 45·82 per cent. CO yields :	Total.	5*a*.	5*b*.	Mean (Corrected for "water-gas reaction").
	CO_2	—	6·20	6·20	3·43	3·40	6·20
	CO	—	39·60	39·60	42·47	42·53	39·72
	H_2	38·81	0·39	39·20	36·10	35·97	38·81
6		From Expt. 3*a*. 35·18 per cent. CO yields :	From Expt. 1*a*. 34·05 per cent. CH_4 yields :	Total.	6*a*.	6*b*.	Mean.
	CO_2	4·76	2·54	7·30	7·58	7·60	7·59
	CO	30·37	28·98	59·35	58·81	58·93	58·87
	H_2	0·30	46·01	45·31	43·51	43·35	43·43
	CH_4	—	2·60	2·60	3·07	3·12	3·09

* The partial pressures in this table are multiplied by 100.

The test mixture, on which to check the calculations, was prepared by mixing these two mixtures in approximately equal proportions. The results are recorded in Table IV and the "observed" and "calculated" values for the products of combustion are compared in Table V. When obtaining the "calculated" values, allowance was made for the fact that for experiments Nos. 8*a* and 8*b* exactly equal parts of mixtures 1 and 7 were not taken.

III.—*Mixtures of Several Combustible Gases with Air, Oxygen being in Defect.*

For this series of experiments, mixtures were chosen in which the speed of uniform movement of flame in a horizontal glass tube 2·5 cm. in diameter was 30 cm. per second. The tube used was 150 cm. long and the flames travelled at a uniform speed over a distance of 100 cm. At a distance of 25 cm. from the open end of the tube, at which the mixtures were ignited, a side-tube was fused with a gas-sampling arrangement attached thereto which enabled a sample of the products of combustion to be secured the moment the flame had passed.

The proportions of inflammable gas required to give a mixture in which the speed of uniform movement of flame, under these conditions of experiment, is 30 cm. per second are: for methane and air 12·50 per cent.; for hydrogen and air 70·20 per cent.; and for carbon monoxide and air 66·78 per cent. Each of these mixtures was inflamed in the manner described and the analyses of the products of combustion are recorded in Table VI. The ratios p_2/p_1 given in that table are calculated from the percentages of nitrogen in the mixtures before and after combustion.

Complex mixtures were now prepared by blending these simple mixtures, either two at a time or three at a time, so as to obtain in them approximately equimolecular proportions of the various inflammable gases. The speed of flame in each of these complex mixtures, as in the simple mixtures under the same condition of experiment, was 30 cm. per second. The products of combustion of these complex mixtures are recorded in Table VII and are compared with the calculated values in Table VIII.

There is in each series of experiments close agreement between the "observed" and "calculated" values for the products of combustion of the complex mixtures, showing that our deductions from the law of speeds of flame in complex gaseous mixtures are correct.

So far as the results of the combustion of complex gaseous mixtures with air (or oxygen) are concerned, therefore, the

TABLE IV.—*Upper Limit Mixtures of Methane, Oxygen, and Nitrogen.*

Description :—		Methane–air.		Methane–oxygen.		Equal parts methane–air and methane–oxygen.	
Analysis of mixture. Per cent.	O_2	18·01		42·88		29·30	
	CH_4	12·85		57·12		33·39	
	N_2	69·14		—		37·31	
Experiment No.		7*a*	7*b*	1*a*	1*b*	8*a*	8*b*
Analysis of products of combustion. Per cent.	CO_2	5·46	5·50	3·18	3·17	3·46	3·49
	CO	8·69	8·64	36·17	36·19	24·77	24·75
	CH_4	0·51	0·51	3·25	3·25	2·04	2·07
	H_2	7·34	7·23	57·40	57·41	35·57	35·50
Ratio p_2/p_1		0·884	0·884	1·34	1·34	1·09	1·09
Partial pressures of individual constituents of products of combustion. Atmospheres.	CO_2	0·0483	0·0486	0·0425	0·0424	0·0376	0·0380
	CO	0·0768	0·0764	0·4846	0·4849	0·2699	0·2698
	CH_4	0·0045	0·0045	0·0435	0·0435	0·0222	0·0225
	H_2	0·0650	0·0649	0·7691	0·7692	0·3876	0·3870

TABLE V.—*Partial Pressures of Products of Combustion.**

		Found.		
	Calculated.	Expt. 8*a*.	Expt. 8*b*.	Mean.
CO_2	4·33	3·76	3·80	3·78
CO	26·78	26·99	26·98	26·98
H_2	39·77	38·76	38·70	38·73
CH_4	2·28	2·22	2·25	2·23

* Multiplied by 100.

TABLE VI.

Mixtures with Air in which the Speed of Flame, under the Conditions of Experiment, is 30 cm. per second.

Inflammable gas :—		Methane.		Hydrogen.		Carbon monoxide.	
Analysis of mixture. Per cent.		O_2 / CH_4 / N_2	18·13 / 12·50 / 69·37	O_2 / H_2 / N_2	6·25 / 70·20 / 23·55	O_2 / CO / N_2	6·89 / 66·78 / 26·33
Experiment No.		9*a*.	9*b*.	10*a*.	10*b*.	11*a*.	11*b*.
Analysis of products of combustion. Per cent.	CO_2	6·09	6·01	—	—	15·02	15·07
	CO	7·74	7·80	—	—	56·07	55·90
	CH_4	0·38	0·42	—	—	—	—
	H_2	6·70	6·61	71·01	71·05	0·84	0·91
	N_2	79·09	79·16	28·99	28·95	28·07	28·12
Ratio p_2/p_1		0·877	0·877	0·813	0·813	0·937	0·937
Partial pressures of individual constituents of products of combustion. Atmospheres.	CO_2	0·0534	0·0527	—	—	0·1407	0·1412
	CO	0·0679	0·0684	—	—	0·5254	0·5238
	CH_4	0·0033	0·0036	—	—	—	—
	H_2	0·0588	0·0580	0·5773	0·5770	0·0079	0·0085
	N_2	0·6937	0·6937	0·2355	0·2355	0·2633	0·2633

TABLE VII.

Inflammable gases :—		$CH_4 + H_2$		$H_2 + CO$		$CO + CH_4$		$CH_4 + H_2 + CO$	
Analysis of mixture. Per cent.		O_2	16·16	O_2	7·05	O_2	16·20	O_2	15·38
		CH_4	10·25	H_2	33·84	CO	10·38	CH_4	8·40
		H_2	9·99	CO	33·39	CH_4	10·01	H_2	9·15
		N_2	63·60	N_2	25·72	N_2	63·41	CO	8·91
								N_2	58·16
Experiment No.		12*a*.	12*b*.	13*a*.	13*b*.	14*a*.	14*b*.	15*a*.	15*b*.
Analysis of products of combustion. Per cent.	CO_2	3·76	3·83	5·18	5·22	9·38	9·21	6·65	6·65
	CO	7·65	7·70	34·83	34·86	13·38	13·38	12·81	12·86
	CH_4	0·41	0·51	—	—	0·23	0·33	0·91	0·86
	H_2	12·72	12·90	29·34	29·18	5·34	5·49	10·25	10·10
	N_2	75·46	75·06	30·65	30·74	71·67	71·59	69·38	69·53
Ratio p_2/p_1		0·845	0·845	0·838	0·838	0·885	0·885	0·837	0·837
Partial pressures of individual constituents of products of combustion. Atmospheres.	CO_2	0·0318	0·0324	0·0434	0·0437	0·0830	0·0815	0·0556	0·0556
	CO	0·0647	0·0651	0·2919	0·2921	0·1184	0·1184	0·1072	0·1076
	CH_4	0·0035	0·0043	—	—	0·0021	0·0029	0·0076	0·0072
	H_2	0·1075	0·1090	0·2459	0·2446	0·0472	0·0486	0·0858	0·0845
	N_2	0·6360	0·6360	0·2572	0·2572	0·6341	0·6341	0·5816	0·5816

TABLE VIII.

Experiment No.		Partial pressures of products of combustion. Calculated (× 100).				Partial pressures. Found (× 100).		
			From Expt. 9*a*. 10·25 per cent. CH_4 yields :	From Expt. 10*a*. 9·90 per cent. H_2 yields :	Total.	12*a*.	12*b*.	Mean (Corrected for "water-gas reaction").
12	CO_2		4·39	—	4·39	3·18	3·24	4·39
	CO		5·57	—	5·57	6·47	6·51	5·31
	H_2		4·81	8·21	13·02	10·75	10·90	12·00
	CH_4		0·27	—	0·27	0·35	0·43	0·39
			From Expt. 10*a*. 33·84 per cent. H_2 yields :	From Expt. 11*a*. 33·39 per cent. CO yields :	Total.	13*a*.	13*b*.	Mean (Corrected for "water-gas reaction").
13	CO_2		—	7·03	7·03	4·34	4·37	7·03
	CO		—	26·27	26·27	29·19	29·21	26·52
	H_2		27·82	0·39	28·21	24·59	24·46	27·20
			From Expt. 11*a*. 10·38 per cent. CO yields :	From Expt. 9*a*. 10·01 per cent. CH_4 yields :	Total.	14*a*.	14*b*.	Mean (Corrected for "water-gas reaction").
14	CO_2		2·18	4·27	6·45	8·30	8·15	6·45
	CO		8·14	5·43	13·57	11·84	11·84	13·61
	H_2		0·12	4·70	4·82	4·72	4·86	3·02
	CH_4		—	0·26	0·26	0·21	0·29	0·25
		From Expt. 9*a*. 8·40 per cent. CH_4 yields :	From Expt. 10*a*. 9·15 per cent. H_2 yields :	From Expt. 11*a*. 8·91 per cent. CO yields :	Total.	15*a*.	15*b*.	Mean (Corrected for "water-gas reaction").
15	CO_2	3·59	—	1·87	5·46	5·56	5·56	5·46
	CO	4·56	—	6·99	11·55	10·72	10·76	10 84
	H_2	3·95	5·28	0·10	9·33	8·58	8·45	8·41
	CH_4	0·22	—	—	0·22	0·76	0·72	0·74

combustion can be regarded as involving the simultaneous but independent burning of a number of simple mixtures of the individual gases with air (or oxygen) in which the proportions of inflammable gas and air (or oxygen) are such that each mixture, if burning alone, would propagate flame with the same speed (under the same conditions of experiment) as does the complex mixture.

The "Relative Affinities" of Methane and Hydrogen for Oxygen.

The observations we have made (which, it should be pointed out, have no bearing on the character of the reactions that are taking place in flames, but refer only to the final effects of those reactions), seem to us to offer an explanation of the apparent greater "affinity" of methane for oxygen than either hydrogen or carbon monoxide possesses which Bone has deduced from his experiments on gaseous combustion at high pressures (*Phil. Trans.*, 1915, [*A*], **215**, 275). In our opinion the methods of calculating the "relative affinities" used in that paper are open to criticism, and we think that the results can be explained in a simpler manner.

In order to make our criticism of the method of calculation clear, it will be necessary to quote the description given in Bone's paper. The theoretical basis for the method of calculation is contained in the following paragraphs (p. 298):

"The possibility of deducing from our bomb experiments a direct comparison between the relative affinities of methane and hydrogen in explosions arose from the fact that the primary oxidation of methane involves a direct transition from $CH_4 + O_2$ to $CH_2(OH)_2$, which later breaks up into, ultimately, $CO + H_2 + H_2O$, without any deposition of carbon. Whence it follows that if mixtures $CH_4 + O_2 + xH_2$ be exploded, the division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (that is, direct oxidation) may be deduced from the proportion of the original methane found intact in the final products, provided always that there is no separation of carbon, which, in fact, is never observed in such circumstances."

"The experimental method consisted, therefore, in exploding a series of mixtures $CH_4 + O_2 + xH_2$, in which the hydrogen and oxygen were initially present in as nearly as possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 8, and determining from the percentage of the original methane remaining intact in each case (1) the oxygen distribution when $x = 2$, and (2) the influence on such distribution of successive equal increments of x up to 8."

The exact steps taken in making the majority of the calculations

from the results of these experiments appear to have been as follows: The partial pressure of the methane burnt is equal to the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion. These products can only arise, according to Bone, from the interaction of equimolecular proportions of methane and oxygen; therefore, the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion is a direct measure of the partial pressure of the oxygen used by the methane "during the extremely short period of actual combustion." Since the partial pressure of the oxygen originally present in the mixture was equal to that of the methane, therefore the partial pressure of the methane found unburnt after explosion must represent the partial pressure of oxygen that was prevented from combining with the methane—because it combined with hydrogen.

Two examples of calculations from experiments with the mixture $CH_4 + O_2 + 2H_2$, recorded in Table IV (*loc. cit.*, p. 299), will suffice to show the method:

Experiment No :—		16.	17.
Partial pressures in gaseous products in atmospheres.	CO_2	0·394	1·164
	CO	4·470	10·910
	H_2	14·320	35·520
	CH_4	0·270	0·555
Per cent. distribution of oxygen deduced from unburnt CH_4.	to CH_4	94·74	95·6
	to H_2	5·26	4·4

Our own calculations from these results, made in the manner described in the preceding paragraph, are: From experiment 16, $\frac{p\ CO_2 + p\ CO}{p\ CO_2 + p\ CO + p\ CH_4} = 94{\cdot}74$ per cent. of oxygen combined with methane, and $\frac{p\ CH_4}{p\ CO_2 + p\ CO + p\ CH_4} = 5{\cdot}26$ per cent. of oxygen combined with hydrogen; and from experiment 17, calculated in the same manner, the corresponding values are 95·6 and 4·4. The identity of our results with those recorded by Bone indicates that we have correctly followed the method of calculation he used.*

The calculations themselves are open to criticism on the score that the results of them cannot but be inaccurate because, (1) the experimental mixtures rarely contained methane and oxygen in exactly equimolecular proportions, and (2) owing to experimental error, the sum of the partial pressures of carbon dioxide, carbon

* Our calculations give the same results as those recorded in the paper in 15 out of the 17 experiments performed in Bomb *A*. The calculations from the experiments performed in Bomb *B* (9 in number) were apparently made directly from the unburnt methane, and not, as in the experiments with Bomb *A*, indirectly from the other products of combustion.

monoxide, and methane after explosion does not balance the partial pressure of methane in the unexploded mixture. In all but one of the twenty-six experiments of the series under discussion, more carbon compounds appear in the products of combustion than can be accounted for by the original methane; sometimes much more, as in experiment No. 23, in which 12·1 atmospheres of methane produced 14·15 atmospheres of carbon compounds.

We are primarily concerned, however, with the theoretical basis for the calculations, which causes Bone to believe that they disclose the manner in which oxygen divides itself between methane and hydrogen "during the extremely short period of actual combustion." It can be accepted as most probable that the primary oxidatiou of methane involves the reactions $CH_4 + O_2 \longrightarrow CH_2(OH)_2 \longrightarrow CO + H_2 + H_2O$. It is doubtful, however, whether this must needs be the only primary reaction. There is evidence from experiments recorded elsewhere in Bone's paper (Table III), that when methane is exploded with less than its own quantity of oxygen, more methane burns than can be accounted for by the reactions $CH_4 + O_2 \longrightarrow CO + H_2 + H_2O$. Bone himself admits the possibility of the primary reaction $CH_4 + O \longrightarrow CH_3(OH)$ taking place when mixtures of methane and oxygen in which the methane is in excess are exploded; the possibility of this reaction occurring when the excess methane is replaced by hydrogen must also be admitted.

If this does happen, and there is no proof that it does not, then the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion does not give a direct measure of the partial pressure of the oxygen used by the methane, for they have not resulted solely from the interaction of equimolecular proportions of methane and oxygen.

We therefore cannot accept the suggestion that Bone's experiments of necessity afford a measure of the "division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (that is, direct oxidation)." Even if they did, which we do not admit, we cannot understand why Bone should conclude that a measure of the "relative affinities" of methane and hydrogen for oxygen is thereby obtained.

The reactions taking place during "the extremely short period of actual combustion" presumably are not instantaneous. They have a finite speed, and that speed will be dependent on the temperature at which they take place. It cannot be assumed that the reactions proceed at one fixed temperature. As Dixon has pointed out in his study of the combustion of mixtures of carbon monoxide and hydrogen (*Phil. Trans.*, 1884, **175**, 623), not only is the tem-

perature at which the reactions in a given " layer " of a gas mixture are taking place altering continuously, but the composition of the mixture is also altering as the reactions proceed, so that "the final division of the oxygen represents the sum or net result of its dividing itself between the two combustible gases in a series of different ratios during a series of successive moments."

In our view, the results of Bone's experiments follow as a natural consequence of the law of speeds of flame in complex gaseous mixtures as exemplified in the present paper. When a mixture of methane, hydrogen, and oxygen, the oxygen being in defect, is inflamed, the methane must of necessity combine with the major portion of the oxygen because the methane–oxygen association that is required to yield the same speed of flame as the hydrogen–oxygen association is the richer in oxygen.

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XLVIII.—*The Quaternary System Ammonium Chloride–Sodium Sulphate–Ammonium Sulphate–Sodium Chloride–Water.*

By ALBERT CHERBURY DAVID RIVETT.

THE results recorded in this paper represent an extension of some measurements originally made in order to ascertain the most suitable conditions for the production of ammonium chloride from ammonium sulphate and sodium chloride in presence of water. The work follows the usnal lines of investigations into quaternary systems comprising reciprocal salt pairs and a solvent. The determination of the solid phase, or phases, has been made by the so-called residue method, the extrapolation from solution through wet solid to dry solid being made in an isotherm which requires three dimensions for its graphical representation. No account has been taken of possible formation of mixed crystals in the solids in equilibrium with solutions. Although variations in the compositions of these solids from those of the pure individual species must of necessity occur (Rivett, *Chem. News*, 1921, **123**, 251), they are certainly very small in all cases coming within this particular system.

It has been decided to record the compositions of all solutions

and residues in weights per cent. There is not yet any general agreement as to the best way of stating results, but this would seem to be the most generally useful method, provided that densities of solutions are also measured. It is a simple matter then to recalculate to any other preferred system on either weight or volume basis. Densities (d_4^t) have been determined to 1 part in 1000 in all cases in this work with the exception of some of the solutions at 80°.

For graphical representation, the pyramidal method (Schreinemakers, *Z. physikal. Chem.*, 1909, **69**, 557) is probably the simplest. The apex of the pyramid corresponds with pure water, the four corners of the base with the respective salts. This involves calculation and plotting of the results in percentages by equivalent, but to save space, the recalculated figures will not be quoted. In order that the surfaces bounding the region of unsaturated solutions may not be too congested towards the apex of the pyramid, the equivalent of water has been taken as that represented by $(H_2O)_{10}$. This throws these surfaces nearer to the base.

The temperatures which have been investigated are 80°, 60°, 40°, 25°, and 0°, whilst in addition one particular point at 70° has been determined and three (condensed) invariant, or five-phase, points as well. A perspective drawing of the pyramid for the most complicated isotherm, that of 25°, is given, but for the others only the orthogonal projections on the base.

Experimental Procedure.

Suitable complexes have been heated in sealed glass tubes to a temperature above that to be investigated and then rotated in a thermostat kept at the latter within 0·02° in the 80°—25° work and within 0·1° in that at 0°. The time of rotation has been from eighteen to thirty-six hours at the higher temperatures and about eight hours at 0°. These times are all far greater than are needed for equilibrium to be attained, especially from 40° upwards. After allowing the solid to settle, the top of a tube was removed and a definite volume of solution drawn into a pipette (previously warmed if necessary) through a cotton-wool filter. The solution was weighed and diluted to a suitable extent for the analytical work.

Chloride radicle has been estimated volumetrically by the Volhardt method; sulphate gravimetrically as barium sulphate; ammonium by the usual distillation procedure. Sodium radicle and water have been calculated by difference. The standards adopted for the volumetric work have been calc-spar and barium sulphate. The results are trustworthy to 1 part in 250 in the

case of solutions. With some of the residues, particularly those separated at high temperatures, a certain loss of water by evaporation was inevitable, but this has never been sufficient to affect the deduction of the solid phases.

The vapour phase has been neglected throughout, or, in other words, the system has been regarded as "condensed."

Thermometers have been compared with instruments standardised at the National Physical Laboratory. The salts used have been commercial "Analysed Chemicals."

Experimental Results.

It is, of course, impossible to say how the radicles are combined in solution, if at all. Instead, however, of expressing results in terms of the separate radicles, the usual practice has been followed of combining them in an arbitrary manner. The arbitrary assumption adopted in this case is that ammonium sulphate and sodium chloride do not occur together in solution, that is to say, they are "incompatible."

It has not been necessary to determine anew all the essential points in the isotherms. For the respective binary systems of salt and water the selected results in the Landolt-Börnstein-Roth Tabellen (1914) have been used. Full use has been made of the work of Dawson (T., 1918, **113**, 679) on the ternary system ammonium sulphate–sodium sulphate–water. Seidell (*Amer. Chem. J.*, 1902, **27**, 52) has determined certain isotherms for the ternary system sodium chloride–sodium sulphate–water, and some of his figures have been adopted. The particular values taken from these authors are marked in the tables. In these tables, *S* signifies solution and *R* residue; also *B* denotes binary, *T* ternary, and *Q* quaternary, systems.

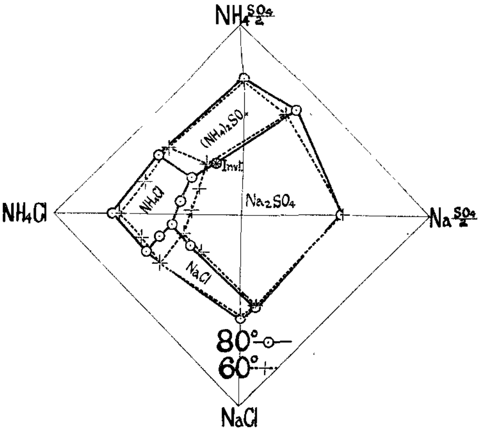
Table I gives the results obtained at 80° and Table II those at 60°. The orthogonal projections of both isotherms are included in Fig. 1.

These isotherms are of the simplest possible type, containing only four saturation surfaces. Each pyramidal model will thus be divisible into twelve regions. The one above the saturation surfaces will include all unsaturated solutions. Below these surfaces there will be four regions such that complexes falling within them will separate into one of the four salts, respectively, and a solution on a surface; five regions in which the separation will be into a pair of salts, capable of co-existing in the solid state, and a solution; two regions in which the separation will be to three salts and a solution.

It will be seen that ammonium chloride and sodium sulphate can exist as solids in equilibrium with any one of a series of solutions, but that ammonium sulphate and sodium chloride cannot.

Dawson (*loc. cit.*) gives 59·3° as the temperature at which a new phase, the hydrated double salt, $Na_2SO_4,(NH_4)_2SO_4,4H_2O$ (which for brevity will be denoted henceforth by " D.S.4 "), appears in the ternary system of these two sulphates and water. A fifth

FIG. 1.



saturation surface therefore begins here and steadily expands as the temperature falls. It will intersect on one side with the ammonium sulphate surface and on the other with that of sodium sulphate. The solution in equilibrium with D.S.4, ammonium sulphate, and sodium sulphate (a four-phase or univariant system) will steadily alter in composition as the temperature falls until a new solid phase, ammonium chloride, appears and the system becomes invariant. This point may be determined very readily by the thermometric method. It is 50·0° ± 0·05° (corr.) and the concentration figures are those given under No. 30 in Table III.

TABLE I.

Temperature 80°.

No.	$d_{4°}^{t°}$.	Percentages by weight. NH₄Cl.	NaCl.	(NH₄)₂SO₄.	Na₂SO₄.	H₂O.	System.	Solid phases present.
S 1	...	39·6	—	—	—	60·4	*B*	NH_4Cl.
S 2	...	—	27·5	—	—	72·5	*B*	$NaCl$.
S 3	...	—	—	48·8	—	51·2	*B*	$(NH_4)_2SO_4$.
S 4	...	—	—	—	30·4	69·6	*B*	Na_2SO_4.
S 5	1·141	29·5	12·0	—	—	59·5	*T*	NH_4Cl,$NaCl$.
S 6	...	27·4	—	23·2	—	49·4	*T*	NH_4Cl,$(NH_4)_2SO_4$.
S 7	...	—	25·3	—	5·0	69·8	*T*	$NaCl$,Na_2SO_4.
S 8	...	—	—	38·9	16·0	45·1	*T*	$(NH_4)_2SO_4$,Na_2SO_4.
S 9	1·2	30·3	7·5	—	6·5	55·7	*Q*	NH_4Cl,$NaCl$.
S 10	...	21·9	9·8	—	9·3	59·0	*Q*	$NaCl$,Na_2SO_4.
S 11	1·197	31·1	3·4	—	12·5	53·0	*Q*	NH_4Cl,$NaCl$,Na_2SO_4.
R 11	...	39·9	17·1	—	22·1	20·9		...
S 12	...	30·5	—	4·9	14·4	50·2	*Q*	NH_4Cl,Na_2SO_4.
S 13	1·247	26·2	—	14·3	12·6	46·9	*Q*	NH_4Cl,$(NH_4)_2SO_4$, Na_2SO_4.
R 13	—	26·5	—	34·5	27·7	11·4		...

TABLE II.

Temperature 60°.

No.	$d_{4^\circ}^{t^\circ}$.	Percentages by weight. NH_4Cl.	$NaCl$.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
**S* 14	1·202	28·7	4·4	—	11·9	55·1	*Q*	$NH_4Cl,NaCl,Na_2SO_4$.
**R* 14	—	33·5	21·7	—	24·2	20·7		...
S 15	...	35·6	—	—	—	64·4	*B*	NH_4Cl.
S 16	...	—	27·0	—	—	73·0	*B*	$NaCl$.
S 17	...	—	—	46·8	—	53·2	*B*	$(NH_4)_2SO_4$.
S 18	...	—	—	—	31·2	68·8	*B*	Na_2SO_4.
S 19	1·118	29·2	7·4	—	—	63·4	*T*	NH_4Cl.
R 19	—	67·7	2·9	—	—	29·4		...
S 20	1·150	24·4	15·7	—	—	59·9	*T*	$NH_4Cl,NaCl$.
R 20	—	63·3	25·4	—	—	21·3		...
S 21	1·132	29·5	—	11·6	—	58·9	*T*	NH_4Cl.
R 21	—	73·9	—	4·0	—	22·2		...
S 22	1·179	23·6	—	25·8	—	50·6	*T*	$NH_4Cl,(NH_4)_2SO_4$.
R 22	—	53·9	—	33·3	—	12·8		...
S 23	1·216	—	24·6	—	5·2	70·3	*T*	$NaCl,Na_2SO_4$.
R 23	—	—	36·9	—	46·5	16·6		...
S 24	1·36	—	—	36·5	16·3	47·3	*T*	$(NH_4)_2SO_4,Na_2SO_4$.
R 24	—	—	—	42·3	45·8	12·0		...
S 25	1·201	17·9	11·5	—	8·7	61·9	*Q*	$NaCl,Na_2SO_4$.
S 26	1·199	25·7	6·2	—	11·3	56·8	*Q*	$NH_4Cl,NaCl,Na_2SO_4$.
R 26	—	39·8	23·9	—	26·2	10·1		...
S 27	1·217	27·8	—	1·6	16·0	54·7	*Q*	NH_4Cl,Na_2SO_4.
R 27	—	50·4	—	0·1	38·8	10·6		...
S 28	1·237	24·2	—	9·7	14·3	51·8	*Q*	NH_4Cl,Na_2SO_4.
R 28	—	49·4	—	2·2	35·8	12·6		...
S 29	1·265	20·4	—	19·3	12·0	48·3	*Q*	$NH_4Cl,(NH_4)_2SO_4$, Na_2SO_4.
R 29	—	25·3	—	32·0	21·5	21·2		...

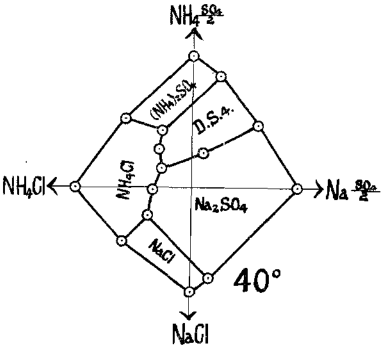
* 70°.

The point is marked Invt. in Fig. 1. On cooling this complex below 50°, ammonium sulphate disappears as a solid phase. Thereafter the D.S.4 *surface meets that of ammonium chloride as well* as those of ammonium sulphate and sodium sulphate. The relations become similar to those of Fig. 2, in which are plotted the results for 40° recorded in Table III.

Here the three-dimensional isotherm will consist of sixteen distinct regions, one above and fifteen below the saturation surfaces.

The type of isotherm remains unchanged until 32·3°, when

FIG. 2.



$Na_2SO_4,10H_2O$ (for brevity, to be referred to as "decahydrate") first appears in the binary system sodium sulphate–water. Below this temperature there will therefore be six saturation surfaces. This is the beginning of the highest complexity reached in the quaternary system. The decahydrate surface increases steadily. At 26·5° (Dawson, *loc. cit.*) in the ternary system ammonium sulphate–sodium sulphate–water an invariant point is reached where D.S.4, sodium sulphate, and decahydrate co-exist with a solution. Below this, these three can exist together only in presence of a solution quaternary in composition, or in other words, only if a degree of freedom be given to the system by the addition of a fourth component. At 25°, the entire quaternary system is

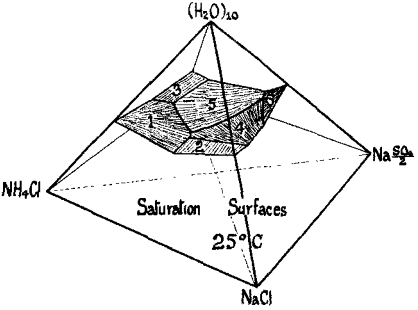
TABLE III.

Temperature 40°.

No.	$d_{4°}^{t°}$.	Percentages by weight. NH_4Cl.	$NaCl$.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
S 30	1·273	18·0	—	19·5	13·0	49·5	*Q*	$NH_4Cl, (NH_4)_2SO_4$, Na_2SO_4, D.S.4.
R 30	—	26·6	—	29·0	25·6	18·8		...
S 31	...	31·4	—	—	—	68·6	*B*	NH_4Cl.
S 32	...	—	26·7	—	—	73·4	*B*	$NaCl$.
S 33	...	—	—	44·8	—	55·3	*B*	$(NH_4)_2SO_4$.
S 34	...	—	—	—	32·5	67·5	*B*	Na_2SO_4.
S 35	1·163	19·4	15·5	—	—	65·0	*T*	$NH_4Cl, NaCl$.
R 35	—	37·0	41·9	—	—	21·1		...
S 36	1·187	19·4	—	24·8	—	55·8	*T*	$NH_4Cl, (NH_4)_2SO_4$.
R 36	—	38·9	—	36·6	—	24·4		...
S 37	1·230	—	23·6	—	6·1	70·3	*T*	$NaCl, Na_2SO_4$.
R 37	—	—	43·8	—	40·1	16·1		...
**S* 38	...	—	—	38·6	10·1	51·3	*T*	$(NH_4)_2SO_4$, D.S.4.
**S* 39	...	—	—	19·8	23·1	57·1	*T*	D.S.4, Deca.
S 40	1·216	20·5	8·3	—	10·7	60·5	*Q*	$NH_4Cl, NaCl, Na_2SO_4$.
R 40	—	29·9	25·5	—	25·8	18·9		...
S 41	1·223	23·9	0·8	—	16·8	58·5	*Q*	NH_4Cl, Na_2SO_4.
R 41	—	45·7	—	—	40·4	14·0		...
S 42	1·245	21·2	—	6·8	16·4	55·6	*Q*	NH_4Cl, Na_2SO_4, D.S.4.
R 42	—	32·1	—	4·7	42·7	20·5		...
S 43	1·242	19·3	—	13·7	12·8	54·3	*Q*	NH_4Cl, D.S.4.
R 43	—	35·3	—	19·8	20·2	24·7		...
S 44	1·256	10·8	—	20·9	10·6	51·8	*Q*	$NH_4Cl, (NH_4)_2SO_4$, D.S.4.
R 44	—	40·8	—	28·1	10·8	20·4		...
S 45	1·274	11·3	—	11·4	19·1	58·2	*Q*	Na_2SO_4, D.S.4.
R 45	—	3·1	—	18·7	53·7	24·5		...

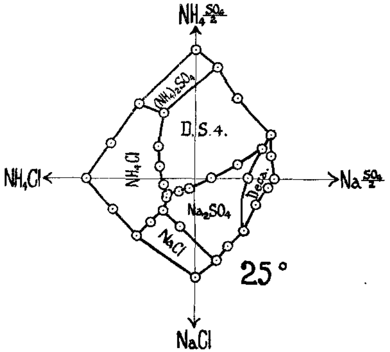
* Dawson (*loc. cit.*).

FIG. 3.



1. NH_4Cl. 2. NaCl. 3. $(NH_4)_2SO_4$. 4. Na_2SO_4.
5. D.S.4. 6. Decahydrate.

FIG. 4.



defined by the figures recorded in Table IV, whilst Fig. 3 represents in perspective (drawn from a photograph of a model) the relative positions of the saturation surfaces.

TABLE IV.

Temperature 25°.

No.	$d_{4^\circ}^{t^\circ}$.	Percentages by weight. NH_4Cl.	$NaCl$.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
S 46	...	28·2	—	—	—	71·8	*B*	NH_4Cl.
S 47	...	—	26·4	—	—	73·6	*B*	$NaCl$.
S 48	...	—	—	43·4	—	56·6	*B*	$(NH_4)_2SO_4$.
S 49	1·216	—	—	—	21·9	78·1	*B*	Na_2SO_4.
S 50	1·123	21·5	8·9	—	—	69·6	*T*	NH_4Cl.
S 51	1·170	15·9	17·1	—	—	67·1	*T*	$NH_4Cl,NaCl$.
S 52	1·127	22·9	—	11·7	—	65·4	*T*	NH_4Cl
S 53	1·188	16·4	—	26·2	—	57·4	*T*	$NH_4Cl,(NH_4)_2SO_4$.
S 54	1·239	—	22·4	—	6·9	70·7	*T*	$NaCl,Na_2SO_4$.
S 55	1·241	—	18·2	—	10·6	71·2	*T*	Na_2SO_4.
S 56	1·250	—	14·0	—	15·2	70·7	*T*	Na_2SO_4, Deca.
R 56	—	—	1·8	—	63·3	34·9		...
S 57	1·218	—	6·2	—	17·6	76·2	*T*	Deca.
S 58	1·212	—	2·1	—	20·5	77·4	*T*	Deca.
S 59	...	—	—	38·3	7·9	53·9	*T*	$(NH_4)_2SO_4$, D.S.4.
S 60	1·290	—	—	25·2	14·3	60·5	*T*	D.S.4.
R 60	...	—	—	33·8	35·5	30·7		...
S 61	...	—	—	13·6	25·1	61·3	*T*	D.S.4, Deca.
S 62	1·262	—	—	6·3	23·1	70·7	*T*	Deca.
R 62	—	—	—	0·7	41·6	57·7		...
S 63	1·196	16·3	13·3	—	5·5	64·9	*Q*	$NH_4Cl,NaCl$.
S 64	1·227	10·9	14·3	—	9·3	65·5	*Q*	$NaCl,Na_2SO_4$.
S 65	1·224	16·8	9·9	—	10·9	62·3	*Q*	$NH_4Cl,NaCl,Na_2SO_4$.
R 65	—	26·2	37·5	—	23·7	12·6		...
S 66	1·229	18·6	5·8	—	14·4	61·3	*Q*	NH_4Cl,Na_2SO_4.
R 66	—	44·0	1·8	—	36·2	18·0		...
S 67	1·230	18·9	4·9	—	15·0	61·3	*Q*	NH_4Cl,Na_2SO_4, D.S.4.

TABLE IV (*continued*).

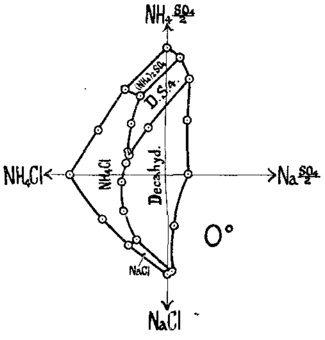
Temperature 25°.

No.	$d_{4°}^{t°}$.	Percentages by weight. NH_4Cl.	$NaCl$.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
R 67	—	30·5	—	14·0	35·0	20·6		...
S 68	1·222	20·7	2·0	—	16·1	61·2	*Q*	NH_4Cl, D.S.4.
S 69	1·214	20·8	—	4·1	14·5	60·7	*Q*	NH_4Cl, D.S.4.
R 69	—	43·0	—	15·0	19·2	22·8		...
S 70	1·216	18·7	—	10·9	11·2	59·2	*Q*	NH_4Cl, D.S.4.
R 70	—	39·2	—	17·7	19·2	23·9		...
S 71	1·236	14·7	—	23·2	7·3	54·8	*Q*	NH_4Cl,$(NH_4)_2SO_4$, D.S.4.
R 71	—	16·0	—	44·5	11·1	28·3		...
S 72	1·237	17·1	3·9	—	16·8	62·1	*Q*	Na_2SO_4, D.S.4.
R 72	—	4·7	—	16·3	55·2	23·9		...
S 73	1·242	15·7	3·0	—	18·8	62·5	*Q*	Na_2SO_4, D.S.4.
R 73	—	3·4	—	8·2	71·3	17·1		...
S 74	1·262	13·4	—	0·1	23·4	63·2	*Q*	Na_2SO_4, D.S.4.
R 74	—	2·2	—	15·8	62·4	19·6		...
S 75	1·293	7·5	—	5·0	24·6	62·9	*Q*	Na_2SO_4, D.S.4.
R 75	—	2·0	—	11·6	64·0	22·4		...
S 76	1·327	2·8	—	9·5	26·4	61·4	*Q*	Na_2SO_4, D.S.4, Deca.
R 76	—	0·5	—	20·4	57·6	21·5		...
S 77	1·324	2·8	—	9·5	26·2	61·5	*Q*	Na_2SO_4, D.S.4, Deca.
R 77	—	0·3	—	12·6	48·9	38·2		...
S 78	1·289	7·5	—	—	27·3	65·2	*Q*	Na_2SO_4, Deca.
R 78	—	1·5	—	—	84·2	14·2		...
S 79	1·259	9·3	3·7	—	21·4	65·6	*Q*	Na_2SO_4.
R 79	—	1·7	0·8	—	84·7	12·8		...
S 80	1·254	8·5	7·4	—	21·6	62·5	*Q*	Na_2SO_4.

The region of unsaturated solutions in Fig. 3 is that between the apex and the surfaces. Below these surfaces there are nineteen separate regions, and in six of them complexes yield one solid phase and a solution; in nine, two solids and a solution; and in four, three solids as well as a solution. The orthogonal projection on the base of the pyramid is given in Fig. 4.

With further fall of temperature the saturation surfaces of D.S.4 and decahydrate steadily expand, whilst that of anhydrous sodium sulphate diminishes. The lowest temperature at which sodium sulphate can exist in the ternary system sodium chloride–sodium sulphate–water, that is to say, the invariant point sodium

FIG. 5.



sulphate–sodium chloride–decahydrate–solution has been found by van't Hoff and Meyerhoffer (*Sitzungsber. K. Akad. Wiss. Berlin,* 1904, 1418) to be 17·9°. Thereafter the sodium sulphate saturation surface lies wholly within the pyramid, that is, this salt can be in equilibrium with quaternary solutions only. At certain still lower temperatures there will then be two four-phase, univariant, quaternary systems, namely, ammonium chloride–D.S.4–sodium sulphate–solution and sodium chloride–sodium sulphate–decahydrate–solution, each of which will become invariant by production of a new phase on further cooling; although which will first reach invariance cannot be predicted. It has not been considered worth while to investigate this part of the system very thoroughly, but some measurements which have been made by the thermometric

TABLE V.

(No. 84—105 at 0°.)

No.	$d_{4°}^{0°}$.	Percentages by weight. NH_4Cl.	$NaCl$.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
S 81	1·237	13·5	11·0	—	11·9	63·6	*Q*	NH_4Cl,$NaCl$,Na_2SO_4 and Deca.
R 81	—	40·0	11·2	—	30·0	17·8		...
S 82	1·237	13·5	11·3	—	11·8	63·5	*Q*	NH_4Cl,$NaCl$,Na_2SO_4 and Deca.
R 82	—	9·0	9·6	—	35·7	45·8		...
S 83	...	13·1	12·1	—	11·5	63·3	*Q*	NH_4Cl,Na_2SO_4, D.S.4, Deca.
R 83	—	21·7	—	0·0	43·5	28·9		...
S 84	...	22·9	—	—	—	77·1	*B*	NH_4Cl.
S 85	...	—	26·3	—	—	73·7	*B*	$NaCl$.
S 86	...	—	—	41·4	—	58·6	*B*	$(NH_4)_2SO_4$.
S 87	...	—	—	—	4·8	95·2	*B*	Na_2SO_4.
S 88	1·133	15·3	11·1	—	—	63·6	*T*	NH_4Cl.
R 88	—	74·1	3·0	—	—	22·9		...
S 89	1·185	10·2	19·9	—	—	69·9	*T*	NH_4Cl,$NaCl$.
R 89	—	52·6	30·2	—	—	17·3		...
S 90	1·131	17·1	—	13·9	—	69·0	*T*	NH_4Cl.
R 90	—	80·0	—	3·9	—	16·0		...
S 91	1·196	11·3	—	28·4	—	60·2	*T*	NH_4Cl,$(NH_4)_2SO_4$.
R 91	—	35·6	—	40·8	—	17·6		...
S 92	1·213	—	25·6	—	1·4	72·9	*T*	$NaCl$, Deca.
R 92	—	—	30·0	—	22·9	47·1		...
S 93	1·094	—	10·7	—	1·5	87·8	*T*	Deca.
R 93	—	—	1·0	—	40·2	58·8		...

TABLE V (*continued*).

(No. 84—105 at 0°.)

No.	$d_{4°}^{0°}$.	Percentages by weight. NH_4Cl.	NaCl.	$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.	System.	Solid phases present.
**S* 94	...	—	—	38·2	4·5	57·3	*T*	$(NH_4)_2SO_4$, D.S.4.
**S* 95	...	—	—	29·4	7·6	63·0	*T*	D.S.4, Deca.
S 96	1·138	—	—	13·4	5·8	80·9	*T*	Deca.
R 96	—	—	—	2·4	37·1	60·5		...
S 97	1·199	10·3	18·4	—	2·8	68·6	*Q*	NH_4Cl,NaCl, Deca.
R 97	—	29·4	26·2	—	10·7	33·7		...
S 98	1·168	14·6	10·1	—	4·6	70·6	*Q*	NH_4Cl,Deca.
R 98	—	33·4	2·1	—	21·7	42·9		...
S 99	1·161	18·8	2·2	—	9·9	69·1	*Q*	NH_4Cl, Deca.
R 99	—	32·4	—	1·7	23·5	42·3		...
S 100	1·175	18·2	—	3·7	10·4	69·7	*Q*	NH_4Cl, Deca.
R 100	—	25·8	—	1·4	24·9	48·0		...
S 101	1·182	17·1	—	6·1	10·0	66·8	*Q*	NH_4Cl, D.S.4, Deca.
R 101	—	19·2	—	16·0	27·8	37·1		...
S 102	1·182	17·0	—	7·0	9·5	66·6	*Q*	NH_4Cl, D.S.4.
R 102	—	20·4	—	22·4	25·2	32·0		...
S 103	1·197	13·8	—	16·5	6·3	63·4	*Q*	NH_4Cl, D.S.4.
R 103	—	33·7	—	20·8	18·9	26·6		...
S 104	1·224	10·5	—	26·7	4·3	58·5	*Q*	NH_4Cl,$(NH_4)_2SO_4$, D.S.4.
R 104	—	20·9	—	45·0	23·1	11·0		...
S 105	1·200	10·8	—	14·4	8·5	66·2	*Q*	D.S.4, Deca.
R 105	—	2·3	—	17·6	35·1	45·0		...

* Dawson (*loc. cit.*)

method are quoted under Nos. 81—83 in Table V. These point to the conclusion that the first invariant point, which is at 11·3°, is that at which the solid phases ammonium chloride, sodium chloride, sodium sulphate, and decahydrate co-exist with a solution (No. 81 or 82). Any attempt to cool this system further results in the disappearance of sodium chloride as a solid phase. A new univariant system of ammonium chloride, sodium sulphate, decahydrate, and solution is then obtained, which at the only slightly lower temperature of 11·0° becomes invariant again (No. 83) owing to the formation of D.S.4 as a new solid phase. This is the lowest temperature at which anhydrous sodium sulphate can exist in the quaternary system. Its saturation surface has become a point.

The whole system has now become simpler, there being again only five saturation surfaces, or, in all, sixteen space divisions in the pyramid. At 0° the relations are those represented in projection in Fig. 5, which is in accordance with the observations recorded in Table V.

The decahydrate region has now become quite a considerable proportion of the total. Below 0°, an ice region will appear, giving for a second time a system with six saturation surfaces. According to Dawson (*loc. cit.*), the lower limit of existence of D.S.4 in the ternary system is — 16·0°, at which temperature D.S.4, decahydrate, and ammonium sulphate co-exist with one and the same solution. After this, the D.S.4 region will be completely quaternary, and presumably it disappears at a sufficiently low temperature, the possible solid phases in the various sections being then ice, ammonium chloride, sodium chloride, ammonium sulphate, and decahydrate. No observations, however, have been made below 0°.

Summary.

The heterogeneous equilibria in the quaternary system ammonium chloride–sodium sulphate–ammonium sulphate–sodium chloride–water between 80° and 0° have been described and illustrated by diagrams (chiefly projections).

THE UNIVERSITY OF MELBOURNE. [*Received, February 6th,* 1922.]

XLIX.—*Studies on Thallium Compounds. Part I. Analytical.*

By Arthur John Berry.

Rabe (*Z. anorg. Chem.*, 1906, **48**, 427) prepared thallic oxide by the oxidation of thallous salts with hydrogen peroxide in alkaline solution, and subsequently described some of its properties (*ibid.*, 1906, **50**, 158; 1907, **55**, 130).

Browning and Palmer (*Amer. J. Sci.*, 1909, [iv], **27**, 379) have described a combined gravimetric and volumetric method for the estimation of thallium depending on the reaction:

$$Tl_2SO_4 + 4K_3Fe(CN)_6 + 6KOH = Tl_2O_3 + 4K_4Fe(CN)_6 + 3H_2O + K_2SO_4.$$

The thallic oxide in these experiments was dried at 200°, and the resulting potassium ferrocyanide in the filtrate was estimated by titration with potassium permanganate after acidifying with sulphuric acid.

In the course of a general investigation on thallium compounds, the author has made numerous experiments on the transformation of thallous sulphate into thallic oxide by oxidation in alkaline solution with potassium ferricyanide. It was found that the above reaction was strictly quantitative with recrystallised thallous sulphate. For example, 50 c.c. of a solution of thallous sulphate yielded 0·478 gram of Tl_2O_3 dried at 100°, the calculated weight being 0·477 gram. In another experiment, in which the thallic oxide was dried by exposure over concentrated sulphuric acid in a vacuum desiccator, the weight of Tl_2O_3 obtained was 0·4775 gram.

The dried precipitate was proved to consist of practically pure anhydrous thallic oxide by dissolving a weighed quantity in sulphurous acid, and estimating the thallium gravimetrically as thallous iodide. From 0·5585 gram of Tl_2O_3, the weight of TlI obtained was 0·8050 gram, the calculated value being 0·8107 gram.

The yield of potassium ferrocyanide as calculated from the titrations with permanganate agreed in general fairly well with the requirements of the above equation, but in some experiments the end-point was difficult to obtain, as the liquid, after being acidified, had a strong green colour. Pure potassium ferricyanide was used in these experiments.

The thallic oxide which was used in the experiments described in this paper was always prepared in this way, but the method was abandoned for quantitative work; the estimations were carried out gravimetrically by weighing as thallous iodide.

Action of Acids on Thallic Oxide.—According to a statement in Abegg's "Handbuch der anorganischen Chemie" (III, i, p. 444) hydrochloric acid reduces this oxide on warming, with evolution of chlorine, whilst sulphuric acid scarcely acts on it in the cold, but on warming reduces it with evolution of oxygen. The experiments carried out by the author do not agree with this.

It was found that when the oxide was dissolved in fairly concentrated hydrochloric acid in an apparatus connected with a U-tube containing potassium iodide solution, and the acid solution boiled, the potassium iodide solution showed no evolution of chlorine from the hydrochloric acid: only a solution of thallic chloride was obtained.

A number of experiments were carried out on the preparation and properties of the thallic sulphates obtained by dissolving the oxide in sulphuric acid and crystallising out the products. According to Strecker (*Annalen*, 1865, **135**, 207), a normal sulphate, $Tl_2(SO_4)_3$, can be obtained from thallic hydroxide and sulphuric acid, but Willm (*Ann. chim. phys.*, 1865, [iv], **5**, 5) obtained only basic sulphates in this way, even when excess of sulphuric acid was used. Marshall (*Proc. Roy. Soc. Edin.*, 1902, **24**, 306) also obtained basic sulphates in which the ratio of Tl to SO_4 was 1 : 1, but in one experiment an acid sulphate in which the ratio of Tl to SO_4 was 1 : 2 was obtained. Meyer and Goldschmidt (*Ber.*, 1903, **36**, 238) have, however, obtained a thallisulphuric acid, $HTl(SO_4)_2,4H_2O$, from a solution of thallic oxide in dilute sulphuric acid.

In the author's experiments, thallic oxide, usually about 3 grams, was treated with excess of sulphuric acid ($5·4N$) in test-tubes heated in a water-bath. When acid more dilute than the above concentration was used, the action was extremely slow. After the oxide had been completely dissolved, the contents were allowed to crystallise, sometimes by allowing the solutions to evaporate over a water-bath, at other times by conducting the evaporations in a vacuum desiccator. The crystals were then dried by pressing on porous plate, and the ratio of Tl to SO_4 was determined. It was found impossible to purify these products, as they are hydrolysed instantly by water. In four different preparations, in which the proportions of thallic oxide to sulphuric acid were varied, but the sulphuric acid was kept in excess of the calculated quantity to produce the normal sulphate, the ratios of Tl to SO_4 were respectively, 1 : 1·055, 1 : 1·13, 1 : 1·025, and 1 : 1·09. It will be

observed that the estimation of the acid radicle was always high, due, doubtless, to the impossibility of completely removing the sulphuric acid by pressing on porous plate.

In only one case was a product obtained in which the ratio of Tl to SO_4 was 1 : 2. Two analyses were made. In the first, the thallium was reduced to the thallous condition by sulphur dioxide before precipitation as iodide, the ratio being 1 : 2·16. In the second case, the reduction was effected by the use of hydroxylamine sulphate, and the value of the ratio was 1 : 2·13. In no case was a normal sulphate obtained. These preparations were almost free from thallous salt, as their reaction towards acidified potassium permanganate was negligible.

A few details may be added with reference to the performance of the analyses. The material was dissolved in dilute nitric or acetic acid, and the sulphate radicle estimated by adding a slight excess of a solution of barium acetate. The thallium in the filtrate was next reduced with sulphur dioxide, the barium sulphate separated, and the thallium precipitated as iodide in the manner recommended by Baubigny (*Compt. rend.*, 1891, **113**, 544). The precipitate of thallous iodide, after being washed first with dilute potassium iodide solution and afterwards with alcohol, was collected on a tared filter and dried over concentrated sulphuric acid in a vacuum desiccator. In some experiments, the procedure was varied by making up the solution to a definite volume, and estimating the metallic constituent in one aliquot part and the sulphate radicle in another.

In the course of this research, other well-known methods of analysis were examined. In particular, a number of experiments were made on the volumetric method of oxidising thallous salts in acid solution with potassium permanganate. In these experiments, the end-point of the reaction was determined with the aid of an electrometric apparatus, consisting essentially of a potentiometer in conjunction with a calomel standard electrode. It was found to be impossible to employ this method in sulphuric acid solution, as precipitation always occurred before the completion of the titrations. When hydrochloric acid was used, the results were to some extent dependent on the amount of thallium in the solution. For example, in a solution containing 1·16 grams of thallous sulphate per litre, the result was 3 per cent. too high when calculated from permanganate which had been standardised with sodium oxalate. With more concentrated solutions, 5·32 grams of the salt per litre, correct results were obtained, but even in such cases the results depend to some extent on the rate at which the permanganate is run in, and on the concentration of the hydro-

chloric acid. Traces of chlorine were perceptible if the permanganate was added too rapidly. These results are in essential agreement with those obtained by Hawley (*J. Amer. Chem. Soc.*, 1907, **29**, 300), who has directed attention to the inaccuracy of the method for very dilute solutions.

Experiments on the Reduction of Thallic Salts.

(*a*) *With Hydroxylamine.*—Reduction to the thallous condition may be easily and quantitatively effected by hydroxylamine either in acid or in alkaline solution with evolution of gas. Experiments were made in order to ascertain whether the reaction takes place according to the equation :

$$Tl_2O_3 + 2NH_2{\cdot}OH = Tl_2O + 3H_2O + N_2O.$$

Preliminary experiments consisted in allowing definite quantities, usually one to two grams, of thallic oxide to react with excess of a 1 per cent. solution of hydroxylamine sulphate, and measuring the volume of gas evolved in an Ostwald apparatus. No great accuracy was expected from these experiments on account of the considerable solubility of nitrous oxide in water.

In every case, the volume of gas obtained was lower than the requirements of the equation. In ordinary cases, the difference between the observed and the calculated volume of gas varied from about 4 to about 8 per cent. When the reaction was carried out in alkaline solution, reduction took place much more rapidly and the volume of gas obtained was still lower. In all cases, qualitative tests showed that reduction was complete. A further experiment was carried out in which excess of thallic oxide was taken relative to hydroxylamine sulphate. Some thallic oxide remained undissolved. When more hydroxylamine sulphate solution was added to make the total quantity equal to the calculated amount, the oxide dissolved completely on warming.

That the reaction really does take place between one molecular proportion of thallic oxide and two of hydroxylamine was proved by a modification of the last experiment. 2·164 Grams of thallic oxide were treated with 25 c.c. of hydroxylamine sulphate solution (0·25 gram of the salt) in presence of excess of a solution of sodium hydroxide. The mixture was heated in a water-bath and frequently shaken. The weight of thallic oxide which remained undissolved was 1·479 grams. Hence the quantity which had reacted with the hydroxylamine sulphate was 0·685 gram. Theory requires 0·695 gram.

Qualitative experiments showed conclusively that when reduc-

tion was carried out in alkaline solution in the cold, traces of nitrite were produced. These nitrite reactions were quite definite even after the solution had been kept for twenty-four hours. On the other hand, there was no evidence of the formation of traces of nitrate. The production of salts of hyponitrous acid was an obvious possibility, especially in view of the work of Hantzsch and Kaufmann (*Annalen*, 1892, **292**, 317), who have investigated the formation of small quantities of salts of this acid when hydroxylamine is oxidised in alkaline solution with certain metallic oxides, such as those of silver, copper, and mercury. Accordingly, tests were made, by adding acetic acid and silver nitrate, for hyponitrite, but no definite reaction was obtained.

(*b*) *With Ferrous Sulphate.*—Reduction of a thallic salt to the thallous condition may be effected completely by an acid solution of ferrous sulphate. When a solution of ferrous sulphate is oxidised with potassium dichromate in presence of sulphuric acid, the end-point of the reaction, as determined in the usual way with potassium ferricyanide, is unaltered in presence of thallous sulphate. Experiments were therefore carried out to ascertain whether reduction proceeds quantitatively in accordance with the equation:

$$Tl_2(SO_4)_3 + 4FeSO_4 = Tl_2SO_4 + 2Fe_2(SO_4)_3.$$

A solution of thallic oxide in dilute sulphuric acid was prepared, containing 0·00957 gram of the oxide per c.c. as determined gravimetrically by the iodide method. Definite quantities of this solution were mixed with known quantities of a solution of ferrous sulphate, heated to boiling, and cooled, and the excess of ferrous salt estimated with a standard solution of potassium dichromate. The weight of thallic oxide calculated from the above equation was 0·00941 gram per c.c.

(*c*) *With Sodium Arsenite.*—Freshly precipitated thallic oxide is completely reduced to the thallous state when it is warmed with a solution of sodium arsenite. Experiments showed that the reaction takes place according to the equation:

$$Tl_2O_3 + As_2O_3 = Tl_2O + As_2O_5.$$

Measured quantities of the solution previously used for the ferrous sulphate experiments were made alkaline with excess of a solution of sodium hydrogen carbonate. Excess of a standard solution of sodium arsenite (approximately $N/10$) was added, and the liquid heated until the precipitate was completely dissolved. The thallium was next precipitated as iodide, the weight of which corresponded with a weight of thallic oxide of 0·00946 gram per c.c. The excess of sodium arsenite was titrated with a standard solution of iodine,

and the weight of thallic oxide calculated from the equation was 0·00949 gram per c.c.

(*d*) *With Copper.*—Finely divided copper reduces a solution of thallic sulphate to the thallous condition on boiling. In an experiment on the solution already referred to, the excess of copper was removed by filtering, and the cupric salt in solution precipitated as oxide. The thallium was then precipitated as iodide, the weight obtained corresponding with 0·00942 gram of Tl_2O_3 per c.c.

It is obvious that the reactions with ferrous sulphate and with sodium arsenite furnish convenient volumetric methods for the estimation of thallium in thallic compounds. It is true that the results, whilst very concordant among each other, are slightly low. In this connexion, it may be recalled that Rabe (*loc. cit.*) has shown that water, when simply boiled with thallic oxide, gives the sensitive iodide reaction for thallous salts. The author has, however, found that if the same specimen of thallic oxide be treated with successive quantities of water, the reaction with potassium iodide becomes gradually fainter and finally almost nil. It would appear probable, therefore, that the phenomenon is more likely to be due to gradual elimination of traces of thallous compound from the thallic oxide rather than to slight reduction, as Rabe considers. Small quantities of thallous impurity would not make a difference, appreciable by ordinary gravimetric analysis, to the percentage of thallium in apparently pure thallic oxide on account of the high atomic weight of the metal.

The author desires to express his sincere gratitude to Sir William Pope for advising him to undertake the study of thallium compounds, and for most kindly allowing him the use of his materials for the purpose; and to Mr. Heycock for the great interest he has taken in the experiments and for many valuable suggestions.

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Artificial Disintegration of the Elements.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 9th, 1922.

By SIR ERNEST RUTHERFORD, F.R.S.

SINCE the development of the atomic theory on an experimental foundation by Dalton, the progress of chemistry has been based on the central idea of the permanency and indivisibility of the atoms of the elements. The whole experience of chemistry for nearly a century had shown clearly that it was impossible to break up the atoms of the elements by the application of ordinary chemical and physical processes. This idea has had to be modified to some extent by the rapid growth of our knowledge during the last twenty years of the inner constitution of the atoms. It is now generally accepted that the atoms of the different elements have all the same general type of structure. At the centre of the atom is a positively charged nucleus of minute dimensions which is responsible for most of the mass of the atom. This is surrounded by a distribution of electrons held in equilibrium by the forces from the nucleus. The electrons occupy rather than fill a region the diameter of which is of the order of 2×10^{-8} cm. The nuclear charge of the atoms follows a very simple rule first clearly brought to light by Moseley. The resultant nuclear charge of an atom is equal to its atomic or ordinal number and varies from 1 "atom" of electricity in the case of hydrogen to 92 atoms in the case of uranium. These ordinal numbers represent also the number of "planetary" electrons, as they have been called, which surround the nucleus of the atom. On this view of the atom, its ordinary physical and chemical properties, apart from its mass, are governed entirely by nuclear charge, for this controls the number and arrangement of the external electrons on which these combining properties mainly depend. The mass of the atom is a property of the nucleus and exercises only a second-order effect on the distribution of the electrons and so on the ordinary properties of the atom. This point of view offers at once a simple explanation of isotopes, which consist of atoms of the same nuclear charge but of different nuclear masses. By the action of light and electrical discharges, we can readily remove one or more of the external planetary electrons from the atom, while by the action of X-rays and swift β-rays we may even eject one of the more strongly bound electrons of the system. In this way, we can effect, in a sense,

a transformation of the atom, but it is merely a temporary one, and a new electron is soou captured from outside, and the atom is as before. The general evidence iudicates that, even if a number of the planetary electrons were removed by suitable agencies, the stability of the nucleus would not be disturbed and the atom would in a short time regain its original structure. In order to effect a *permanent* change in the atom, it appears to be necessary to disrupt the nucleus itself. When once a charged unit of the nuclear structure is removed, the nuclear charge is altered permanently, and there is no evidence that this process is reversible under ordinary experimental conditions.

The discovery of the instability of the radioactive elements was the first severe shock to the idea of the permanency of all atoms. This radiating property is, however, confined mainly to the two heaviest elements, uranium and thorium, and their long series of descendants, and is only shown by two other elements, potassium and rubidium, aud then only to a minor extent. Apart from these exceptions, the great majority of the atoms appear to be highly stable structures, and to remain unaltered under ordinary conditions in this earth for periods of probably thousands of millions of years.

The property of radioactivity belongs to the nucleus, and is shown generally by the emission of a swift α-particle or helium nucleus and, occasionally, a swift electron from the nucleus. The number and velocity of emission of these particles appear to be quite uninfluenced by the most powerful physical or chemical agencies, and to be an inherent property resulting from the instability of these very complex nuclei.

These results show clearly that the nuclei of heavy atoms contain both positively charged helium nuclei and negative electrons, *and lead to the general view that the complex nuclei of all atoms* are built up of hydrogen and helium nuclei and electrons. It is *also generally supposed that a helium nucleus itself is a* secondary unit composed of four hydrogen nuclei and two electrons. If this be the case, we may suppose the nuclei of all atoms to be composed ultimately of hydrogen nuclei, or "protons," as they have been termed, with the addition of negative electrons.

Radioactivity has thus not only provided us with the key of the structure of the elements, but has at the same time given us in the swift α- and β-particles a powerful method of probing the inner structure of the atom. By firing α-particles into the atoms of matter, we are able, by following the deflexions of the path of the α-particle, to find out the magnitude and law of the forces close to the nucleus and to form some idea of the dimensions of

the latter. The general results suggest that the diameter of the nucleus of heavy atoms is of the order of 4×10^{-12} cm. or about 1/5000 of the diameter of the whole structure of the atom. The law of the inverse square of repulsion between electric charges is found to hold for a considerable region surrounding the nucleus. No doubt the size of the nuclei of light atoms is even smaller, and in the case of helium appears to be of the order of 5×10^{-13} cm. It is thus clear that the nuclei of atoms, although of very complex structure, are of exceedingly small dimensions.

It is probable that the forces which bind together the components of the nucleus are exceedingly powerful, and that consequently a large amount of energy will be required to disrupt its structure. The swift α-particle from radium and thorium, which is by far the most concentrated source of energy known to us, seems the most likely agent to succeed in an attack on the strongly-bound nucleus. The α-particle is expelled from radium with a velocity of about ten thousand miles per second, and thus has a speed twenty thousand times greater than that of a swift rifle hullet. Mass for mass, its energy of motion is four hundred million times greater than that of the bullet.

Whilst no doubt an α-particle fired directly at a heavy nucleus may penetrate its structure, its energy may at that stage be too small to cause a disruption. The attack on the lighter atoms is much more promising, for the repulsive forces are so much smaller that the α-particle may still retain much of its energy on entering the nuclear structure.

Before, however, considering experiments on this question, it is desirable to say a few words on the collision of α-particles with hydrogen nuclei, where no question arises of the disruption of the atom. When α-particles pass through hydrogen gas, there are occasional close collisions between the α-particles and the hydrogen nuclei, resulting in the appearance of high speed H-nuclei. These H-particles travel abont four times the distance of the bombarding α-particle, and can easily be detected by the scintillations they produce on a zinc sulphide screen. From the ordinary principles of mechanics, the maximum speed given to an H-nucleus is 1·6 times that of the colliding α-particle, whilst the maximum energy communicated to it is 0·64 of the energy of the α-particle. It is found that the number of these swift H-atoms is far in excess of that to be expected if it be supposed that the α-particle and hydrogen nucleus hehave as point charges for the very small distances involved in these violent collisions. In addition, the variation of the number with the velocity of the α-particle and the number shot off at different angles with the α-particle differ

markedly from the results to be expected on the simple point theory.

It seems clear that not only has the α-particle a structure, but that the law of force at very short distances is entirely different from that of the inverse square. As a result of a careful investigation, Chadwick and Bieler recently concluded that the results of the collisions could be explained by supposing that the α-particle —to which the complexity is ascribed—behaves like a spheroid of axes 8×10^{-13} and 5×10^{-13} cm. Outside this surface, the law of the inverse square applies, but the forces increase so rapidly when the H-nucleus enters the spheroidal surface that it is rapidly turned back. This model of the helium nucleus is, no doubt, quite artificial, but it gives us some idea of its probable dimensions and the extent of the region in which new and powerful forces come into play.

We should consequently anticipate that, in a close collision of a swift α-particle with the nucleus of atoms more complex than that of hydrogen, the ordinary laws of force would break down when the distances apart became very small. It must be remembered that gigantic forces come into play in these nuclear collisions, and only very stable structures may be expected to survive the encounters.

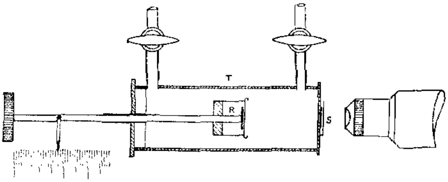
The first observation which has to do witb the main subject of my lecture was made some years ago. When the α-rays from a strong radioactive source pass through dry gases like oxygen or carbon dioxide, a small number of weak scintillations are observed on a screen beyond the range of the α-particles. These " natural " scintillations are believed to be due to atoms of hydrogen coming from the source, and probahly result from a slight hydrogen contamination of the source during exposure to the radium emanation. If, however, dry air is substituted for oxygen or carhon dioxide, the number of scintillations is increased three or four times. This additional effect was found to be due to the presence of nitrogen, and was shown in a correspondingly greater degree by chemically prepared nitrogen. By suitable arrangements, it was found that the particles causing these scintillations were bent by a magnetic field to about the extent to be expected if they consisted of swift, charged H-atoms. It seemed probable from the beginning that these additional H-atoms, which appeared only in dry nitrogen and not in oxygen or carbon dioxide, must have their origin in a disintegration of the *nitrogen nucleus by collision with a swift α-particle.*

With the original counting arrangements, the scintillations were small in number, weak in intensity, and difficult to count with accuracy. Further progress has depended mainly on improvements in the counting microscope, with the object of increasing

the intensity of the scintillations and the area of zinc sulphide screen under observation. By the use of wide-aperture objectives and special eyepiece lenses of low magnifying power, the counting of these scintillations has become much easier and more definite.

Dr. Chadwick and Dr. Hartridge have recently constructed for me a microscope which takes in the maximum field of view for the magnification required. With its aid, we are able to observe an area of zinc sulphide screen of about 40 sq. mm. and at the same time have bright scintillations. The rays from the objective are turned through a right angle by a totally reflecting prism in order to protect the counter from the direct γ-radiations from the intense source. On account of the probability variations in the number of particles falling on the zinc sulphide screen, a large number of scintillations must be counted to obtain the true average. For example, if 400 scintillations are counted in all, the average

Fig. 1.



probability error is $\sqrt{400}$, or 5 per cent. of the total number. We cannot hope in the experiments detailed later to obtain results of an accuracy of more than 5 or 10 per cent. unless a very large amount of time and energy is spent in counting a great number of scintillations. Apart from the difficulty of accurate counting, the actual numbers found in these experiments are only approximate.

We shall now consider the methods adopted to investigate in more detail the effects observed in nitrogen and to test whether other elements behave in a similar way. The apparatus (see Fig. 1) required is of the simplest character and merely consists of a brass tube, *T*, 3 cm. in diameter, provided with stopcocks by means of which dry gases may be circulated. At one end of the tube is a hole covered with a thin silver plate. The zinc sulphide screen, *S*, is fixed 1·3 mm. away from the opening, leaving a slit in which absorbing screens of mica can be inserted. The radioactive source, *R*, is fitted on the end of a rod so that its distances from the screen can be varied at will. In order to reduce

the luminosity due to the β-rays from the source, the whole apparatus is placed in a strong magnetic field. It may be of interest to give a few details in illustration of the magnitude of the effects to be expected under different conditions. Suppose that the radioactive source, consisting of a brass disk coated on one side with an invisible layer of radium-*C* corresponding in γ-ray activity to 40 milligrams of radium, is placed 3·5 cm. from the screen and that a current of dry hydrogen is passed through the apparatus. Suppose the stopping power of the materials between the source and the zinc sulphide screen corresponds to 20 cm. of air, that is, it would suffice to stop an α-particle of range 20 cm. in air. The passage of the α-particles, which in this case have a range of 7 cm., through the hydrogen liberates a large number of high speed H-atoms, which produce scintillations on the screen. Their number with the microscope described is so great—thousands a minute—that it would be impossible to count them without reducing the activity of the source. As additional absorbing screens of mica are added, the numbers fall off rapidly, and for an absorption, say, of 30 cm., not a single H-scintillation can be observed per minute. A similar effect is shown if oxygen is substituted for hydrogen and a thin strip of paraffin wax or other hydrogen-containing material is placed over the source. The number of H-scintillations observed for a given absorption depends only on the amount of hydrogen, and is quite independent of chemical combination. This is to be expected, for the forces required to set the H-nucleus in rapid motion are enormous compared with the weak forces involved in chemical combination. We thus conclude that, for α-particles of range 7 cm., no H-atoms from hydrogen in the free state or in chemical combination can be detected for an absorption greater than 30 cm. of air.

The oxygen, which gives no scintillations, is now replaced by dry air. At once we observe for an absorption of 30 cm. more than 100 scintillations per minute when for hydrogen we did not observe one. By adding mica screens we find that the scintillations cease for an absorption of 40 cm. It is clear that these particles from nitrogen have a greater range than free H-atoms bombarded by α-rays, so that the effect observed beyond 30 cm. cannot be ascribed to any hydrogen impurity in the nitrogen.

The air is now replaced by neutral oxygen, and thin foils of say copper, iron, silver, gold of stopping power corresponding to about 3 cm. of air are successively placed over the source. Not a single H-atom can be observed for an absorption of 30 cm. A foil of aluminium is substituted and at once the number of scintillations jumps to more than 100 per minute. Some of the scintil-

lations are very bright, and we find that some of the particles are so swift that the absorption must be increased to 90 cm. before the scintillations vanish. It is clear that aluminium must give rise to a number of very long-range particles.

It is seen that if we examine the number of scintillations beyond the range of ordinary H-atoms, we are quite independent of any possible contamination of hydrogen in the material under examination. This is a great advantage, for we need not worry about the purity of the material as regards hydrogen. In this way, Dr. Chadwick and I have examined a large number of elements to test whether they emit particles of range more than 32 cm. When the element was not available, a compound of the element with an "inactive" element like oxygen was used. The material in the form of a fine powder was dusted on a thin gold foil, an adhesive film being used so that the average absorption of the material corresponded to from 3 to 4 cm. of air, and was then exposed to the source of rays. With the exception of helium and neon and argon, all the elements have been tested up to atomic weight 40. No element of atomic weight greater than phosphorus, 31, was found to give any effect, although it should be said that only a few of the elements of higher atomic weight have so far been examined.

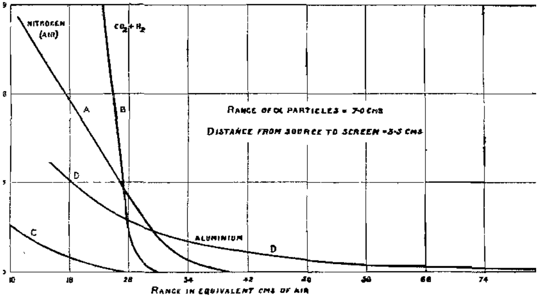
A list of the elements examined in this way, from lithium to sulphur inclusive, is given in the following table. The second column gives the number of scintillations per minute per milligram activity of the source, namely, radium-*C*, for an absorption of 32 cm. of air. These numbers afford only a rough comparison of the effects given by different elements, for the conditions of the experiment, for example, the thickness and distribution of the film of material, varied from element to element. The fourth column gives the approximate range of the particles.

Element.	Material.	No. of particles per min. per mg. for the microscope used.	Maximum range of particles in cm. of air.
Lithium	Li_2O	—	—
Glucinum	GlO	—	—
Boron	B	0·15	*ca.* 45
Carbon	CO_2	—	—
Nitrogen	Air	0·7	40
Oxygen	O_2	—	—
Fluorine	CaF_2	0·4	over 40
Sodium	Na_2O	0·2	*ca.* 42
Magnesium	MgO	—	—
Aluminium	Al, Al_2O_3	1·1	90
Silicon	Si	—	—
Phosphorus	P (red)	0·7	*ca.* 65
Sulphur	S, SO_2	—	—

In addition to these, the following elements of higher atomic weight were examined: chlorine as $MgCl_2$; potassium as KCl; calcium as CaO; titanium as Ti_2O_3; manganese as MnO_2; iron, copper, tin, silver, and gold in the form of metal foils. In no case were any particles observed of range greater than 32 cm. of air. The question whether any of these elements give particles of range less than 32 cm. has not been examined.

It will be seen that the elements which give scintillations for an absorption of 32 cm. are boron, nitrogen, fluorine, sodium, aluminium, and phosphorus. The numbers for boron and sodium were distinctly less than for the other elements.

FIG. 2.



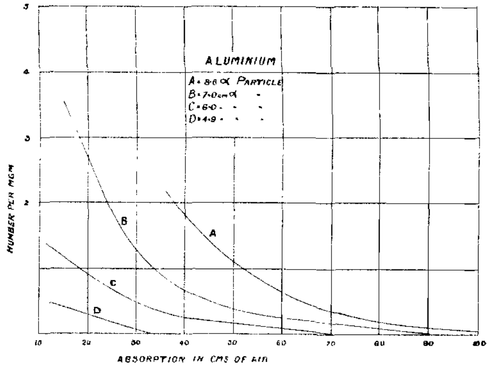
ABSORPTION CURVES IN NITROGEN AND ALUMINIUM.

The variation in the number of scintillations as the absorption in the path of the rays increases from 10 cm. is shown in Fig. 2. The source of α-rays is in all cases radium-*C*. Curve *A* shows the effect in nitrogen (air) where the maximum range is 40 cm. Curve *B* is the corresponding absorption curve for a mixture of hydrogen and carbon dioxide, about 1 volume of H_2 to 1·5 of CO_2, which gives the same stopping power as air for α-rays. The number of scintillations due to hydrogen is very great in this case from absorptions less than 20 cm., but falls off rapidly, and none could be distinguished beyond 30 cm. Curve *C* gives the natural effect when the air is replaced by dry oxygen. This is seen to be small compared with that observed in nitrogen. Curve *D* shows the

effect when an aluminium plate of 3·5 cm. stopping power is placed over the source and the air replaced by oxygen. It is seen that the particles liberated from aluminium are able to penetrate a much greater thickness than the particles from hydrogen or nitrogen.

It is a matter of great interest to find how the absorption curves for these long-range particles vary with the velocity of the bombarding α-particles. This has been examined for two typical elements, nitrogen and aluminium, and the results for the latter are shown in Fig. 3. It was found that to a first approximation

FIG. 3.



the maximum range of the particles liberated from an element was proportional to the range of the bombarding particles. In all cases, the number of scintillations falls off rapidly as the velocity of the α-particles is decreased. The effect of velocity is specially marked in aluminium, and few, if any, particles are observed when the range of the α-particles is reduced to 4·9 cm. of air. The effect shown in curve *D* (Fig. 3) is almost entirely due to the "natural" scintillations from the source. When we remember that the decrease in velocity corresponding with the reduction of the range of an α-particle from 7 cm. to 4·9 cm. is only 11 per cent., we see how rapidly the number falls off with lowering of the velocity. It seems likely that no disintegration can be effected in the case

of aluminium if the velocity of the α-particle falls below a certain critical value. This is not easy to prove conclusively, but, if correct, indicates that the α-particle must have a certain critical energy to release an H-atom from the nucleus.

A very striking result was observed in the case of aluminium. It is to be expected that the liberated particles should for the most part be projected in the direction of the bombarding α-particles. Actually, it was found, however, that nearly as many were shot in the backward as in the forward direction. No evidence of such an effect was observed in the case of the nitrogen particles. The other elements have not yet been examined from this point of view, but we should expect an element like phosphorus, which gives rise to long-range particles, to show a similar effect. A possible explanation of this striking result will be given later.

Nature of the Expelled Particles.

It can easily be shown that the long-range particles liberated from the elements are deflected by a strong magnetic field. By the adoption of special methods, it has been found possible to compare the amount of deflexion of these particles with that shown by the swift H-atoms produced when α-particles pass through ordinary hydrogen. It was found that the particles from nitrogen were deflected to about the same extent as the H-particles from hydrogen, and behaved in all respects like swift H-atoms carrying a positive charge. It seemed likely from the first that the corresponding particles from fluorine, phosphorus, and aluminium would also prove to be H-atoms liberated from the nuclei at speeds depending on the nature of the element and the velocity of the impinging particle. This has been confirmed in recent experiments by Dr. Chadwick and myself by a method similar to that employed for nitrogen. The bending of the particles in a magnetic field was determined for an absorption greater than 32 cm. of air, in order that the experiments should not be complicated by the possible presence of hydrogen contamination in the material under examination. The experiments were not easy on account of the small number of particles present under the experimental conditions and it was found necessary to devise a special microscope with a large field of view to carry out the investigation at all. The experiments were all in accord with the view that the particles from fluorine, phosphorus, and aluminium are swift atoms of hydrogen, and we may conclude that in each case an H-atom is liberated from the nuclei of these elements. The maximum speed of ejection of the H-atom from the different elements can be

estimated approximately by assuming that the law connecting the velocity and range of the α-particle holds also for the H-atom. According to this rule, the velocity is proportional to the cube root of the range.

It has been calculated and confirmed by experiment that the maximum speed communicated to a free H-atom by a head-on collision with an α-particle of velocity V is $1{\cdot}6V$, whilst its range in air is about 28 cm. Consequently, the maximum velocity of the H-atom from nitrogen of range 40 cm. is $1{\cdot}8V$ and for aluminium of range 90 cm. $2{\cdot}37V$. The α-particle communicates 0·64 of its energy to a free H-atom in a direct collision, and it can be calculated that all H-atoms which have a range greater than about 56 cm. are projected with energy greater than that of the bombarding α-particle. In the case of aluminium, the maximum energy of the H-atom is 1·4 times that of the incident α-particle. This is a very interesting result, showing that in some cases there is actually a gain of energy as a result of the disintegration of the aluminium nucleus. We must therefore conclude that at any rate for all collisions in which the liberated H-atom has a range greater than 56 cm. of air, a part of the energy of the H-atom is derived from the disintegrated nucleus. This is analogous in some respects to the well-known gain of energy in the escape of an α-particle from a radioactive nucleus.

It must be borne in mind that the amount of disintegration effected by the α-particles is on an excessively minute scale. When a particle from radium-C passes through aluminium, it probably passes through the electronic structure of about 100,000 atoms, but only about two α-particles in every million get near enough to the inner nucleus to effect the liberation of an H-atom We know that the collected α-particles from 1 gram of radium give rise to 163 cubic mm. of helium per year. If we suppose that all the α-particles from 1 gram of radium were fired into aluminium, the amount of hydrogen liberated by the disintegration of the aluminium nuclei could not be more than 1/1000 of a cubic millimetre per year. The amount of hydrogen liberated under possible experimental conditions is thus almost beyond the means of detection by ordinary chemical methods. It has only been possible to study the disintegration by the use of such a delicate method that each H-atom set free produces a visible scintillation on a zinc sulphide screen.

Mechanism of Disintegration.

From a study of radioactivity, it has been surmised that the α-particle or helium nucleus of mass 4 is one of the units of which the atoms are built up. The experiments referred to in this lecture give the first definite proof that the hydrogen nucleus also is one of the units of the structure of some of the lighter elements. It is of interest to note that H-atoms are only liberated from elements the atomic masses of which are given by $4n + 2$ or $4n + 3$, where n is a whole number. Elements like carbon and oxygen, the atomic masses of which are given by $4n$, are not affected. This is shown in the following table :—

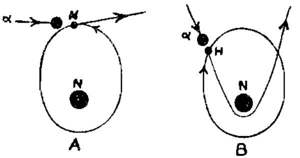
Element.	Mass.	$4n + a$.	Element.	Mass.	$4n + a$.
Boron	11	$2 \times 4 + 3$	Sodium	23	$5 \times 4 + 3$
Nitrogen	14	$3 \times 4 + 2$	Aluminium ...	27	$6 \times 4 + 3$
Fluorine	19	$4 \times 4 + 3$	Phosphorus ...	31	$7 \times 4 + 3$

This result is to be anticipated if the nuclei of these elements are built up of helium nuclei of mass 4 and hydrogen nuclei. In order to account for the liberation of an H-atom from these elements, it is natural to suppose that the H-nuclei are satellites of the main nucleus. If the satellite is not too close to the latter, the α-particle in a close collision is able to give the satellite sufficient energy to allow it to escape from the system. It is to be anticipated that the H-satellites are closer to the nucleus in the case of aluminium than in the case of nitrogen, and that consequently more energy is necessary in the case of aluminium to effect their release. It is of interest to note that the chance of liberating a swift H-atom from nitrogen is not more than 1/20 of the chance of setting a free H-atom in corresponding motion. This indicates that it is probably only within certain prescribed limits of velocity of the satellite and position with regard to the central nucleus that the liberation of the satellite is possible.

We have already referred to the fact that the H-atoms from aluminium appear to be released in all directions. Actually, however, the velocity in the backward direction of the α-particles is distinctly less than in the forward direction. Such a result at first suggests that the α-particle acts the part of a detonator to the aluminium nucleus and that the energy of the escaping fragments is mainly derived from the nucleus. I think, however, that the following explanation is more probable and in better agreement with experiment. If we suppose that the H-satellite is describing an orbit round the central nucleus, the direction of escape will depend on the relative position of the α-particle and nucleus at the moment of the close collision with the satellite.

In the collision shown in Fig. 4, *A*, for example, the H-atom will escape in the forward direction of the α-particle; in the collision (Fig. 4, *B*) the H-atom will describe an orbit round the nucleus and escape in the backward direction. The velocity imparted to the residual nucleus in the forward direction is much greater in the latter than in the former case. Such a view assumes that the forces between the positively charged satellite and nucleus are attractive instead of repulsive very close to the nucleus. This change of sign of the forces seems very probable at short distances from the nucleus, for otherwise it is difficult to understand how a positively charged complex nucleus can hold together.

FIG. 4.



Another consequence of some interest follows from the possibility of releasing H-atoms from light elements. It is generally supposed, although it is very difficult to obtain direct proof, that the helium nucleus is composed of four hydrogen nuclei and two electrons. In this combination, there is a loss of mass and this is ascribed to the very close combination of the structural units. On modern views of the relation between mass and energy, it follows that the energy liberated in the formation of a helium nucleus is more than three times the energy of the swiftest α-particle from radium. We should consequently not expect to be able to break up a helium nucleus with an ordinary α-particle, and this is in agreement with experiment as far as it has gone. In fact, the helium nucleus would appear to be the most stable of all nuclei.

Since, however, in the case of nitrogen, for example, we are able to release an H-atom by means of a slow α-particle, it seems clear that the H-satellite is not bound nearly so closely in the nitrogen nucleus as in the case of the helium nucleus. The change of mass due to the emission of energy in binding the H-satellite should consequently be much less than in the case of helium. The mass of the satellite should not differ much from the free H-nucleus of mass 1·0077 in terms of O = 16.

If it be supposed that the nitrogen nucleus is made up of three

helium nuclei of total mass 12 and two hydrogen nuclei, the mass of the nitrogen atom should not be exactly 14·00, but more nearly 14·01. In the case of the light elements, it appears probable that the effective mass of the protons composing the nuclei will vary in different atoms from about 1·007 to 1·000, depending on the closeness of the combination. Consequently, we should expect that the whole-number rule found by Aston, which appears to hold for atomic masses to about 1 in 1000, would be departed from if measurements could be made with yet greater accuracy.

The next question that arises is whether any other particles besides that of hydrogen can be released by α-ray bombardment. Some time ago, I found that when radium-*C* was used as a source a small number of bright scintillations were observed, which had a maximum range in air of about 9 cm. It was natural at first to suppose that these were due to a new type of α-rays from the radioactive source. The effect, however, of aluminium screens in reducing the range of these particles led me at first to believe they were generated in the volume of the gases used, namely, nitrogen and oxygen. By comparing the bending of these rays in a magnetic field with that of H-particles from hydrogen, I concluded that they must be atoms of mass about 3 carrying two positive charges. Later experiments have brought home to me the untrustworthiness of this method of fixing the source of the radiation on account of the marked variation in thickness of films of metal foil. Using a more direct and simpler method, I have recently convinced myself that, at any rate in the case of oxygen, the particles have their origin in the radioactive source and not in the volume of the surrounding gas. Under such conditions, the comparative method of estimating the mass of the particles is no longer trustworthy. Whilst a large amount of experiment will be required to fix definitely the nature of the radiation, the general evidence indicates that it consists of particles of mass 4 which are projected from the source and represent a new mode of transformation of radium-*C*.

By the methods outlined we can only hope to detect particles which travel a distance greater than the primary α-particles. If, however, a disintegration of an element should occur in which a massive particle is liberated, it is quite probable that the latter may have a range shorter than the α-particle. To examine cases of this kind, we can utilise the beautiful method developed by Mr. C. T. R. Wilson for showing the trails of ionising particles. Some experiments of this kind by a modified method have been made by Mr. Shimizu in the Cavendish Laboratory. A number of photographs showing well-marked forks near the end of the path

range have been observed. Until, however, these photographs are accurately measured up and compared with one another, it is difficult to be certain whether or not these branching tracks can be explained by collisions of the α-particle with the nuclei of nitrogen or oxygen. It seems clear, however, that the nuclei involved can travel considerable distances through the gas before being absorbed. If a large number of photographs be taken, it should be possible to settle definitely whether any collisions involving the disruption of atoms occur and to determine the probability of their occurrence. This direct method of attack of the problem, whilst laborious, should give very valuable information ou this point.

It appears not improbable that the α-particle may occasionally be able to disrupt a helium atom from a complex nucleus like carbon or oxygen, which are believed to be composed of three or four helium nuclei respectively. The fact that the mass of these atoms is nearly an integral multiple of the helium atom suggests that the helium nuclei are bound together with much weaker forces than the H-components of the helium nucleus itself. If the structure of the complex nucleus, say, of oxygen is such that the α-particle may communicate a considerable fraction of its momentum and energy to a single component, we should expect such disintegration to occur. It is also possible that charged particles of mass about 2 or 3 may exist as secondary building units of the complex nuclei of some elements, but so far no definite evidence of their liberation has been obtained.

I have so far confined my remarks to the disintegrating effects of swift α-rays, but it is important to consider whether the swift β-rays or energetic γ-rays from radium are able to produce any effect. We have found that neither β- nor γ-rays appear to have the power of giving sufficient energy to a free H-atom in ordinary hydrogen to detect it by the scintillation method, and consequently still less should we expect these rays to liberate a swift H-atom from a complex nucleus. It is, however, possible that these agencies, and particularly γ-rays of very short wave-length, may be able to liberate an electron and lead in this way to a change of its atomic number. Unless, however, the resulting atom is unstable and breaks up with the emission of a swift particle of the α-ray type, it will be difficult to be certain of such transformations. It should be noted that Slater has shown that α-rays are able to excite some very penetrating rays in their passage through ordinary matter. There is some evidence that such high-frequency radiation can only arise from the nuclei of atoms. If this be the case, it may be possible that the α-rays in some cases

lead to a liberation of a β-particle from the nucleus and a consequent transformation. This effect, however, must be on a very small scale.

Many attempts have been made in the past to test whether the ordinary atoms can be disintegrated by special agencies. The late Sir William Ramsay, with his characteristic instinct for choosing the best line of attack, made a number of experiments on the effect of the α-rays of radium on matter and concluded that he had obtained evidence of the production of neon and the liberation of lithium from copper. These conclusions have not been confirmed by subsequent investigators, and in the light of the experiments described in this lecture it seems very doubtful whether the amount of transformation, even if it occurred, would be sufficient to be detected by ordinary chemical methods such as were employed.

Many instances have been recorded of the appearance of helium in discharge tubes, and it has been suggested that helium is a product of the transformation of the electrodes by the action of the intense electric discharges. The most notable experiments in this direction have been made by Collie, but the subsequent detailed investigations by Strutt did not confirm his conclusions. It is exceedingly difficult to prove that the appearance of helium is not due to its occlusion in the electrodes and liberation by the intense heating of the discharge. Similarly, many observations have been made of the steady liberation of hydrogen from electrodes. Winchester, who examined this effect in detail with thin aluminium electrodes, found that hydrogen was released until the electrodes were entirely dissipated. It is very difficult to believe that this hydrogen is a product of the transformation of aluminium when we remember the great energy of the α-particle required to effect it. As in the case of helium, it seems more probable that the hydrogen was originally absorbed in the electrodes.

Whilst it is dangerous to be dogmatic on these points, the general evidence indicates that the atoms as a whole are such stable structures and the nuclei are held together by such powerful forces that only the most concentrated source of energy like the α-particle is likely to be effective in an attack on such well-protected structures. Even when disintegration takes place, it is on an exceedingly minute scale, and only a few α-particles in a million are effective. If we had charged atoms available of ten times the energy of the α-particle from radium, we could probably penetrate the nuclear structure of all atoms and occasionally effect their disintegration.

L.—*A Theoretical Derivation of the Principle of Induced Alternate Polarities.*

By Arthur Lapworth.

The great advances towards a definite theory of valency which have recently been made by Thomson (Silliman Lectures, 1903; *Phil. Mag.*, 1921, [vi], **41**, 510), Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 763), and Langmuir (*ibid.*, 1919, **41**, 868, etc.) have been followed by the appearance of numerous papers applying electrical conceptions to the reactions of carbon compounds. Of these may be specially mentioned the papers of Fry (*Z. physikal. Chem.*, 1911, **76**, 385, 398, 591; and numerous communications to the *J. Amer. Chem. Soc.*), of Robinson (T., 1916, **109**, 1030, 1038; 1917, **111**, 959, etc. Also, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 17), and of Conant (*J. Amer. Chem. Soc.*, 1921, **43**, 1703). The suggestions of Prins (*Chem. Weekblad*, 1918, **15**, 571) and of Vorländer (*Ber.*, 1919, **52**, [*B*], 263) appear to be based on conceptions of strains which are not very clearly electrical in origin.

Recently the present author pointed out that a general law is apparent in the reactions of carbonyl compounds, and deduced from it a wider generalisation which he termed the "principle of induced alternate polarities" (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1). The principle had reference to the apparent electropolar characters of the atoms in a chain at the moment of chemical reaction and was deduced without having recourse to any hypothesis of the mechanism of reaction. (Compare *Ann. Reports*, 1919, **16**, 87—89, where a summary of views expressed up to that time by Prins, Vorländer, and Lapworth is given; also Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, iii, 1.)

In his paper to the Manchester Society (*loc. cit.*, pp. 3 *et seq.*) the author pointed out that his views agreed more closely with those of Robinson, whose influence in modifying his attitude towards such questions was gratefully acknowledged, than with those of Fry, to whose figures his own sometimes bore a close and natural resemblance. He differed from Robinson, however, in some important respects, and, in particular, he did not regard it as necessary, or usually even desirable, to assume the occurrence of reactions within closed circuits, but preferred, as a rule, to postulate what may be termed, "reactivity induced from a distance," much as polarity may be induced in an uncharged body by the proximity of a charged one.

No one who carefully studies these apparently divergent views can fail to be struck with the fact that at many points they tend

to shade into one another or can fail to suspect that they might all be referred to a single fundamental principle or combination of principles, and in the present paper it is hoped to indicate where these may be looked for and how they may be brought into line with modern electronic theories such as those of Lewis, Langmuir, and Thomson (1903 and 1921). As some of the fundamental points connected with the discussion and the general mode of reasoning were indicated by the author more than twenty years ago, he now ventures to refer in the first instance to the communications in which this was done.

It was suggested (T., 1901, **79**, 1265, *et seq.* Compare also P., 1901, **17**, 93, *et seq.*) that the laws of change in carbon compounds are the (mathematically) necessary results of the operations of the laws of valency applied to the migration of the point or condition of free valency arising from a dissociation akin to ionisation.* It was noted, however, that what may now be termed a "simplifying factor" must also be operating and this was stated in the following form: "*The state of dissociation which leads to isomeric change exists, in general, only once in the molecule at any instant.*" These considerations led at once to the "αγ-rule" for a chain of atoms such as carbon, and indicated that the alternate atoms in such a chain might be expected to exhibit similar powers of acting as the seats of ionic reactivity; or, to use a phraseology now familiar in such connexions, the alternate atoms might be expected to show similar "polarities."

Consideration of a great variety of data such as those to which the author directed attention in his paper on the "Latent Polarities of Atoms, etc." (*loc. cit.*), has made it evident that induced alternate polarities frequently become manifest which cannot be explained by the "migration" of a "whole" free valency; but by extending similar conceptions to include the migration of "partial" valencies with polar characters, it appears possible to construct a general explanation which is also remarkably consistent with the modern electronic views.

Modified Lines of Development of the "αγ-Rule."

It is assumed in the development that each atom in its organic chemical combination can be associated with a given (maximal) number of bonds or valency lines; that, whilst any atom may not have more than this maximal number associated with it, it may have less; and, lastly, that the total number of these bonds

* The idea of the "wandering" of a free bond arising from the process of ionisation had previously been utilised by Wislicenus in his work on "Tautomerie" (Ahrens-Sammlung), by Knorr, and by Brühl, with the object of explaining tautomerism (compare T., 1904, 85, 48, footnote).

or valency lines (whole+fractional) in any part of a molecule remains constant unless there is definite reason to postulate that some have passed to or from another part of the molecule or to or from the surroundings.

This last proviso will appear inconsistent with the partial valency formulæ used by Thiele, and with the great majority of others now quite usually seen in works on organic chemistry; but these are conventional, mathematically faulty, and incapable, without modification, of furnishing an explanation of the "principle of induced alternate polarities."

A glance at the Figures, I and II, will make clear the differences between the usual notation and that used by the present author. Certain missing partial valencies are denoted by the sign, ×, where in the usual notation these would appear as real partial valencies; they will hereafter be referred to as "virtual." Attachment of a distinguishing sign, such as ×, to some of the free partial valency lines in many of the formulæ now in common use, would serve equally well.

A "virtual valency" may be defined by the statement that the sum of the "real" and "virtual" bonds and valencies attached to any atom in its organic chemical combinations is equal to the usual "maximal" valency of the atom as above defined. It is *not to be confused with a "residual" or "latent" valency*, which is an excess, or rather, an unshared quantity, of what, with a "virtual" valency, is in defect.

Now the conditions laid down at the beginning of this section permit of a great variety of modes in which valencies may be readjusted after a disturbance, some of these modes being dependent on the original disturbance and others not. In order to limit the modes in such a way as to exclude forms which the organic chemist, out of his experience, would consider purely fanciful, it is necessary to introduce such a "simplifying factor" as the author enunciated in 1901. (Compare italics on p. 417 of present paper.) The author now prefers to state it in the following extended form:

When any disturbance takes place in the number of shared or free valencies which are associated with an atom in its normal state of combination, then a constraint is usually set up and the atom strives to regain its normal condition. This may lead to a redistribution of valencies elsewhere; but in the consequent changes due to the propagation of the strain along any part of the molecule the strains at all points in that part taken together cannot exceed the original constraint in that part. (The chances of a second disturbance arising independently at another point in the same molecule are small unless the first is so prolonged as to assume a static character, and in the following pages the results of a single initial disturbance only are considered.)

The first part of this assumption is obviously an attempt to apply, so far as it seems possible to do so, the "Principle of Least Action" which has been variously enunciated by Maupertius, Le Chatelier, and others. A first approximation for the calculation of the values of the constraint and strains is indicated a little later on.

The most general relations to which the author desires to direct attention in the first instance can be deduced most readily from a consideration of possible "consequent" changes in part of a molecule, such, for example, as the part, $A_1 \ldots A_4$, in the central formula in either of the Figs. I or II. These central formulæ are supposed to represent the molecules in their normal, or "resting" conditions. A_0, A_1, etc., are the symbols of atoms and A_0 is supposed to be joined directly to A_1, but is figured with all bonds, atoms, etc., otherwise associated with it in such a way as to make it possible to defer for the present any discussion of what it is precisely that is happening in that part of the molecule, as that is a large question independent of the immediate issue. The + and — signs which are attached to the atoms in the central formulæ are in anticipation of the conclusions arrived at in later portions of the present paper and, as in the author's earlier paper (*Mem. Manchester Phil. Soc.*, *loc. cit.*), denote the "relative latent polarities" of the atoms; the atom, A_0, is the "key-atom" and, as formerly, is indicated by attaching a dot to its polar sign.

The molecule, represented in each case by the central formula, is assumed to suffer a "constraint," the primary effect of which on the part of the molecule below (A_0, etc.) is solely to alter the magnitude of the bond which attaches A_1 to the atom A_0. It is required to determine what secondary or "consequent" readjustments in the honds and valencies attached to the atoms in the chain, $A_1 \ldots A_4$, may take place without departing from the conditions laid down at the beginning of this section.

A full bond is for generality assumed to be divisible into three equal parts.

The curved arrows indicate the directions of movement of the partial valencies to or from the bond, A_0 A_1.

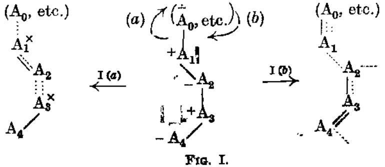


FIG. I.

Case I (Fig. I). Where the constraint is such that the bond between A_0 and A_1 is (I*a*) decreased or (II*b*) increased by (two) partial valencies, respectively (I*a*) passing to, or (I*b*) proceeding from, the system (A_0, etc.) or the exterior, and hence the total of the bonds and valencies attached to the atoms in the chain, $A_1 \ldots A_4$, suffers a corresponding decrease or increase, respectively.

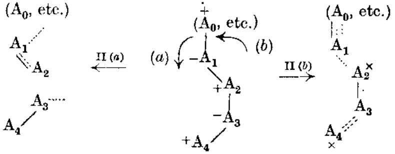


FIG. II.

Case II (Fig. II). Where the constraint is such that the bond between A_0 and A_1 is (II*a*) decreased or (II*b*) increased by (two) partial valencies, respectively (II*a*) passing to, or (II*b*) proceeding from, the chain, $A_1 \ldots A_4$, itself; and hence the total of the bonds and valencies attached to the atoms in the chain $A_1 \ldots A_4$ undergoes no change.

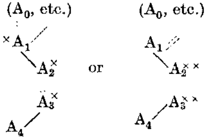
It will be clear that there are theoretically four distinct modes * in which the change in the bond, A_0 A_1, may be effected. In deciding what are the probable forms that the part of the molecule below (A_0, etc.) may assume, as a consequence of the occurrence of each of the four modes, the postulates above laid down have been applied, together with the "simplifying factor." In using the latter it has been assumed, as a first approximation, that the magnitude of the constraint is proportional to the change in the magnitude of the bond, A_0 A_1, and that the strain at each atom is proportional to the change in the number of "free" real valencies or of "virtual" valencies which are attached to it,† the strain being reckoned as positive in all instances.

The relation postulated between "constraint" and "strain" provides, for example, some reasonable premise for understanding why it is not permissible to assume that the atom A_1 in Fig. I(*a*) can be restored after the constraint, towards its original valency

* Cases where new rings are formed are not considered here, though as recent work on intra-annular tautomerism indicates, they may arise far more frequently than has hitherto been suspected.

† In reality the strain associated with a new real free valency varies with the element, and probably in the order C>N>O. For a new virtual valency the order is inverted, and probably O>N>C>H.

by borrowing one or two partial valencies from, say, the bond between A_2 and A_3; for such a process would lead to such structures as



respectively, in the former of which the strain (calculated on the basis that one full free bond or one new full "virtual" valency corresponds with unit strain) is $4 \times \frac{1}{3}$ and in the latter is $6 \times \frac{1}{3}$, whilst the original constraint at A_1 was only $2 \times \frac{1}{3}$. The constraint in the part (A_0, etc.) is not considered.

Now with the foregoing provisions it can be shown, best algebraically, that the only possible modifications of the system, $A_1 \ldots A_4$, are as follow:

Case I(*a*). They are such as have only "virtual" valencies, and these on the "odd" atoms only [unless any of the "even" atoms originally (central formula) had real "free" (latent) valencies, in which case these may diminish].

Case I(*b*). They are such as have only new real "free" valencies, and these on the "even" atoms only.

Case II(*a*). They are such as have only real "free" valencies, and these on the "odd" atoms only.

Case II(*b*). They are such as have only "virtual" valencies, and these on the "even" atoms only [unless any of the "odd" atoms originally (central formula) had real "free" (latent) valencies, in which case these may diminish].

The central formulæ in Figs. I and II are denoted without any free valencies on the atoms, $A_1 \ldots A_4$, and additional figures would be required to cover the considerable variety of possibilities. The complications which are indicated within the square brackets in the immediately preceding paragraphs may work out in a variety of ways according as the atoms with latent valencies are readily deprived of their valencies or not. As will be shown later, there is reason to believe that oxygen and nitrogen, the elements of most frequent occurrence in carbon compounds with latent valencies, adhere very firmly to their valencies; and even with the halogens there appears to be no reason to suppose their free valencies ever lead to the complications in question. Where these complications come into operation, then of course the "αβ-rule" and not the "αγ-rule" will obtain (compare T., 1898, **73**, 457).

The formulæ to left and right in Figs. I and II may therefore be regarded as general expressions for the results of some possible changes in a chain, $A_1 \ldots A_4$, in which the atoms in the "resting" states of the molecule (central figures) have no "free" (latent) bonds or valencies, or, at least, none which is brought into operation as the result of the constraint; they are the "activated" forms (Robinson, *Mem. Manchester Phil. Soc.*, 1921, **64**, ii, 17). The principles indicated in the figures must apply whatever be the precise physical interpretation attached to the chemist's bond or valency line, providing that it has the properties assumed in deducing the relations with which the figures correspond. The necessary simplifications of the figures for the case where a bond is assumed to be divisible into two parts only will readily be made out, as also will modifications thereof, such as, for instance, those in which the strain is not propagated from its original point or is propagated without the distribution (between two atoms) which, for the sake of generality, is suggested in the figures. Extensions to cases where double bonds are present or to those in which the constraint is sufficient to lead to complete disruption of the bond between two atoms will be self-evident.

Interpretations Based on Modern Electronic Views of Valency.

The author, in compiling all previous papers, had in mind the older view that bonds and valencies denoted something of the nature of tubes of force, and it is possible to make out a good case for such a conception even at the present time when chemical combination is coming to be generally accepted as associated with a sharing of electrons by the atoms. It is, however, necessary to bear certain points clearly in mind. For instance: if the laws of valency assumed at the beginning of the preceding section hold quite strictly for the tubes of force, then it has to be assumed that in each atom, considered in its organic combinations, there is a constant number of tubes of force shared by its nucleus and its electrons, and these are included in the symbol for the atom.

Thus, if in Figs. I and II each whole or partial bond or valency line is assumed to stand for a certain number of Faraday tubes which are joining electrons in one atom to the nucleus of its neighbour, then the new "real" free partial valency lines in the formulæ to left and right would represent Faraday tubes proceeding outwards to the surroundings, and the "virtual" valencies would denote tubes proceeding outwards from nuclei. The former would be associated with negative fields and the latter with positive ones. It is thus not difficult to perceive that the arrangement of

+ and − signs in the central formulæ are just those which would be suggested by a study of the reactions of the compounds, and we have a theory which is apparently a generalised form of that proposed by Conant (*loc. cit.*) to explain some reactions of carbonyl compounds.

There is, however, another way of interpreting such figures, to which the author's attention was first directed by Professor J. B. Cohen in a private communication (October 9th, 1921), the relevant part of which may be quoted :

" Why do you split up your bond into three partial valencies rather than two ? If you took two it would fit in with the Lewis-Langmuir atom and your partial valency might represent one electron."

The present author would not wholly abandon the conception of a partial valency line as denoting tubes of force, especially for interpreting the extreme manifestations of the induced polarity phenomena, such as, for example, its effect on the order of acidity of the cresols, which is not easy to understand on the "electron-migration" view alone. But the results displayed in the preceding section must apply either to Faraday tubes or to electrons, or to both, providing only that they obey the laws of valency as defined and limited in that section.

Nevertheless it at once becomes apparent on applying Professor Cohen's suggestion to the interpretation of partial valency formulæ such as have been used latterly, for example, by Robinson and by the present author (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1, 17, and other places indicated in the latter paper), that a remarkably consistent application of modern electronic theory to carbon compounds has already been developed and was only awaiting such a suggestion before taking definite form.

Thus, by limiting the subdivisions of the single bond to two parts (electrons), denoting appropriate valencies as " virtual " * (that is, as indicating missing electrons), and replacing Robinson's looped latent valency signs for nitrogen and oxygen by ordinary free valencies (unshared co-valency electrons), interpretations of reactivity and chemical change appear which are the most striking agreement with modern electronic views. But it would also seem to follow that these views must admit, and Thomson's already appear to do so, of a certain amount of elasticity in the conception of " duplets " as the minimum number of electrons required for, at least, sub-stable atomic attachments. The broad rules of reactivity and substitution in the aliphatic and aromatic series, the

* For example, all those free valencies attached to atoms with + signs in the author's paper.

basic properties of heterocyclic compounds such as pyridine, pyrrole, and glyoxaline, and other problems of equal general interest receive explanations of a satisfying kind in terms of electronic properties *of the atoms of the elements.*

The transformations required to follow the points to which attention was directed in the last paragraph are so simple as to be, in most cases, almost self-evident to any who are familiar with these modern views, and they will not be dealt with in detail here. In the present communication, discussion of this aspect of the general question will be confined to a consideration of the function of the "key-atom" in inducing alternate polarities, and the interpretation of the results in the preceding sections on the assumption that a partial valency shall denote one electron.

It will be evident, in the first instance, that an atom with a "virtual" partial valency is one which has been deprived of one electron; that an atom, which in the "activated" form of the molecule has a new "real" free partial valency, is one which has one more unshared electron than it has in the resting state of the molecule. An atom of the former kind will tend to be associated with a positive field and will be able to unite directly with atoms of the latter kind, which will tend, also, to be associated with negative fields, usually more intense than the positive fields of the other type (compare Briggs, T., 1908, **93**, 1564; 1917, **111**, 253; 1919, **115**, 278). The propagation of the "constraint," then, as a rule (see Figs. I and II) consists simply in the movement of electrons in an atom [say A_2, Fig. I(*a*)] from one shared position to another. Carbon atoms in their normal organic chemical combinations have, of course, eight electrons in their outer shells, all shared; if, in the activated forms of the molecule one is denoted as having a "virtual" partial valency, then it has only seven electrons in its shell; if denoted with a real free partial valency, then it has eight electrons in its shell, but one of these electrons is unshared.

Such a conception, however, seems certainly to require that atoms may be held together, momentarily at least, by one electron only in common. Although the three chief exponents of the modern electronic theories appear to agree that a single shared electron is an unstable form of union, it is not definitely excluded, and Thomson seems to admit the possibility in several places (*Phil. Mag.*, 1921, [vi], **41**, 521), for PCl_5, and p. 538, where he says "the two cells would be united only by a single electron which *might quite likely* be insufficient to hold them together" (the italics are the present writer's).

Now assuming that the "negative key-atom," $\dot{A}_0$ in Fig. I, is operating merely in virtue of a tendency to a variation in the

number of electrons which it shares with the atom A_1, then we may surmise that

(*a*) A_0 should be an atom with a variable co-valency.

(*b*) A_0, if it can function as in Fig. I(*a*), should be an atom which readily *falls* in co-valency.

(*c*) A_0, if it can function as in Fig. I(*b*), should be an atom which readily *rises* in co-valency.

(*d*) A_0 should in any case be an atom which, when it varies in co-valency, adheres strongly to its electrons—and, in particular, more strongly than carbon adheres to its electrons.

Now the atoms of oxygen and nitrogen certainly have the properties (*a*), (*b*), and (*c*), and all to a well-marked degree, when these elements occur in their so-called " bivalent " and " tervalent " states respectively (compare Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 927). The halogens exhibit similar properties, but, it may fairly be said, to a less marked degree (fluorine is not here considered). The author has already pointed out that " bivalent " oxygen and " tervalent " nitrogen are by far the most effective (negative) " key-atoms " and that (" univalent ") chlorine appears to exert, although to a much less marked extent, a somewhat similar " polarising " influence (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 5). Moreover, the order of the affinity of the three elements, oxygen, nitrogen, and carbon, for the electrons in their outer shells (" octets "), is no doubt the order of the proximity of the electrically neutral atoms to the stable arrangement in the neon and this indicates the descending order: $O > N > C$ (compare Briggs, *Phil. Mag.*, 1921, [vi], **42**, 449, 450).

Hydrogen, which appears to exert a slight " polarising influence " of the opposite kind (" positive "), would have to come under Case II (Fig. II); but as it is difficult to see how the Rutherford hydrogen atom could share more than two electrons with another atom, it seems necessary to suppose that here only Case II(*a*) applies: that is to say, that hydrogen, acting as " key-atom," does so by a partial dissociation from its partner, to which it abandons one of the electrons it previously shared with it. This is at least entirely consistent with the crude conception of the formation of hydrion in which a combined hydrogen atom drops both electrons, or with the modified view (which the author prefers), namely, that the dropping of one electron by a combined hydrogen atom is the precedent to the ionisation of acids. In the same connexion may be recalled the experiments of Langmuir and others which have furnished proof of the separate existence of free, neutral hydrogen atoms; that is, of hydrogen atoms with but one electron each.

It will be evident that on an electron-distribution diagram, even

more simply than on a force-field diagram, a satisfactory explanation of the "principle of induced alternate polarities" may be worked out by combining the relations discussed in the previous sections of the present paper with the Lewis-Langmuir-Thomson theories of chemical combination. It is not difficult to perceive many directions in which the conceptions suggest new lines of advance in organic chemical theory, but it is impossible within the scope of a short communication to enter into detail.

Before concluding this paper, it appears worth while to attempt to summarise more obvious possible causes of the "constraint" postulated in the earlier pages. Briefly these would appear to be:

(*a*) Absorption of thermal or radiant energy, leading in the first instance to redistributions of atomic attachments, usually at the atoms with variable co-valencies.

(*b*) Ion formation, by dissociation, at the "key-atoms."

(*c*) Ion formation by association, as, for instance, by the formation of a complex ion by union of the molecule, at the "key-atom," with a simple ion.

(*d*) Non-ionic association with other uncharged molecules, which occurrence, like (*b*) and (*c*), would be likely to upset the balance of forces and lead to new distributions of the electrons or of the tubes of force or, of course, of both.

(*e*) Tendency to certain molecular distributions of affinity.

As an instance of what is meant under the last heading may be mentioned that inspection of a very large number of the most acceptable formulæ based on the conjugation theory of Thiele seems to indicate that there is a definite tendency in carbon chains to something like an even distribution of valency; for example, forms such as $=A_1-A_2\equiv$ tend to arrange themselves as $=A_1=A_2=$. Now the presence of an oxygen or a nitrogen atom at the end of such a system would almost certainly facilitate the occurrence of such a rearrangement owing to the readiness with which these atoms vary in their co-valencies, and at the same time the order of the polarities of the atoms in the system would be determined by the greater tendency for the oxygen or nitrogen atom to retain the maximal number of electrons in its outer shell. In such a case, evidently, the constraint does not originate at the "key-atom," but the result is the same as if it did originate there. This conception, *mutatis mutandis*, is likely to apply for atoms other than oxygen or nitrogen, and is one to which the author attaches very great importance, especially, but not only, in its application to static forms; it would appear to receive immediate and striking application in connexion with molecules having alternate single and double linkings and to *cyclo*aromatic compounds in

particular, especially as Thomson has already pointed out that the most suitable arrangement of the benzene molecule is that in which the pairs of atoms in the ring share electrons in threes, and not in twos and fours alternately (*Phil. Mag.*, 1921, [vi], **41**, 535).

In conclusion, the author desires to emphasise two points: (1) that whilst the interpretation of a partial valency as an electron can be reconciled in the most striking manner with present-day formulæ and reactions as pictured by organic chemists, it would be premature wholly to abandon the force-field view, which is clearly related to it and which in some cases seems better fitted to account for the facts; (2) that, as illustrated in Figs. I and II, it is not the mere weakening or strengthening of a bond that determines the order of the induced polarities in a chain and consequently the modes in which the atoms in the chain react, but rather, whether or not the excess (or defect) in the bond is made up from (or passes to) the chain itself.

The author wishes to express his thanks to Professor J. B. Cohen for the suggestion (p. 423) which promises to be so fruitful.

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LI.—*An Explanation of the Property of Induced Polarity of Atoms and an Interpretation of the Theory of Partial Valencies on an Electronic Basis.*

By WILLIAM OGILVY KERMACK and ROBERT ROBINSON.

IN recent times it has become more and more evident that the graphical formulæ employed by organic chemists to represent the constitutions of chemical individuals are expressions which inadequately symbolise the properties of substances, and from time to time efforts have been made to introduce additional systems of notation corresponding with more or less definite theoretical ideas. Thus the sign adopted by Thiele to denote the existence of conjugation of ethylene linking involves the theory of residual affinity which is almost but not quite identical with that of partial valencies of definite alternately positive and negative polarity as formulated by one of us in order to develop a more convenient representation of the ethylene–nitrogen conjugated system. This theory of partial

valencies equivalent in the sum to the normal valencies from which they are derived has also been applied to the explanation of intramolecular transpositions and of the nature of aromatic homocyclic and heterocyclic types. Similarly, Flürscheim developed a system of exhibiting the now well-recognised alternate effect in chains of atoms by means of thick and thin lines showing augmented and diminished affinities, and Vorländer has used + and − signs with almost the same implication. Michael was perhaps the most important pioneer in emphasising the importance of the influence of the electrical polarity of atoms and groups in molecules, and Lapworth's theory of induced latent polarity of atoms, which, starting from a key-atom of recognised polarity, are alternately *positive and negative in a chain, combines and extends the views of* Flürscheim and of Michael and has proved extremely useful in collating the data accumulated in connexion with such problems as orientation and the mechanism of reactions. Again, Werner has found it necessary to introduce modifications in the conventional representation of the nature of " onium " salts and of " complex " or co-ordinated compounds generally, and the application of his methods has been extended with striking success to many related types, for example, the triphenylmethane and azine dyes and oxonium salts of the anhydropyranol or pyrylium class. Finally, the behaviour of the now numerous isolated radicles such as triphenylmethyl is not well expressed by formulæ with a normal free valency bond, and some kind of partial saturation of the latter by the unsaturated atoms which occur in the molecules of all these substances has frequently been postulated.

Whilst all these theories and their corresponding devices of symbolisation have proved serviceable as working hypotheses, the connecting link in the form of a common physical basis is lacking, and it is the object of the present communication to suggest that such may be found in the Thomson and Lewis-Langmuir theory *

* The suggestions of Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20**, 453) and of Abegg (*ibid.*, 1904, **39**, 330) should undoubtedly be mentioned as clearing the ground for the later recognition of the stability of the electron octet, but in the development of modern electronic views of the nature of valency by far the most influential worker has been Sir Joseph Thomson (Silliman Lectures, " Electricity and Matter," 1903 : *Phil. Mag.*, 1904, [vi], **7**, 237; 1906, [vi], **11**, 769; 1921, [vi], **41**, 510), whose theory of the nature of the chemical bond comprises all the features which are really essential to the interpretation of the symbols employed by organic chemists. The benzene formula given on p. 437 has already been put forward by Thomson. Ramsay expressed the electrical view of chemical combination in a form particularly adapted to appeal to chemists (T., 1908, **93**, 778), and in connexion with the possibility that one electron may be shared by more than two atoms (and vice versa) (see p. 433), Lodge (*Nature*, 1904, **70**, 176) has made sugges-

of the atom and of valency which we employ in the simplified form in which it was expounded by Langmuir at the Edinburgh meeting (1921) of the British Association for the Advancement of Science.

1. *General.*

The outstanding feature of Langmuir's theory which is adopted in the sequel is the explanation of the nature of chemical combination and the recognition of the tendency to form stable octets of electrons in the case of those elements (except hydrogen) which most commonly occur in carbon compounds. With Langmuir, we take a single bond to mean the sharing of two electrons by the atoms connected and a double bond the sharing of four. We desire, however, to suggest that the facts of organic chemistry are best interpreted if it be assumed in addition that it is possible for contiguous atoms to share one or three electrons. In the case of a triple bond, it is thought that the sharing of six electrons, although possible, represents an unstable condition, and the tendency will be for one of the atoms (carbon or nitrogen) to complete its octet in a more stable configuration. It may be recalled that Langmuir has already suggested the deformation of the octet in order to preserve the tetrahedral environment of the carbon atom, and in our view it is the number of electrons, and not a precise definition of their supposed arrangement in space, which is of vital significance.

2. *Co-valence and Electro-valence.*

It would seem that a sharp distinction between these two types of valency is not possible, and our views on this subject are precisely those which have already been clearly expressed by Briggs (T., 1921,

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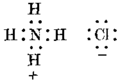
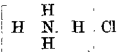
tions which are so relevant to the subject of the nature of partial valency that two sentences may be quoted :—

"On any view electrons are supposed to repel and be attracted with a force varying as the inverse square of the distance, and this is only consistent with a very large number of lines of force radiating from each and starting out in every direction equally."

"When opposite charges have paired off in solitude, every one of these lines starts from one and terminates on the other constituent of the pair, and the bundle or field of lines constitutes a full chemical bond; but bring other charges or other pairs in the neighbourhood, and a few threads or feelers are at once available for partial adhesion in cross directions also."

The following references to the papers of Lewis and of Langmuir may be given: G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; I. Langmuir, *Proc. Nat. Acad. Sci.*, 1919, **5**, 252; *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543; 1920, **42**, 274; *Science*, 1920, **51**, 605. Compare also W. Kossel, *Z. Physik*, 1920, **1**, 395.

119, 1879). It is obvious that the Thomson and Lewis-Langmuir theory (I) of the nature of ammonium chloride is precisely that which Werner developed on purely chemical grounds (II).

(I.)  (II.) 

No difficulties are experienced in applying similar expressions to complex quaternary ammonium salts such as the canadine metho-salts, whereas such formulæ as NH_3 HCl lead to anomalies.

3. *Polar Character of Atoms in Combination.*

An atom is called negative which is surrounded by a stable octet or which tends to attract electrons so as to make up a stable octet. The octets are the more stable the less the electrons are restrained by being shared with other atoms and also the smaller the atomic weight of the element. The tendency to form an octet is the greater the more nearly it is already formed. Conversely, a disintegrated octet tends to further disruption, and atoms surrounded by such unstable systems tend to lose electrons and are positive in polar character. The positive nature of hydrogen implies that a stable condition is reached when no electrons surround the nucleus.

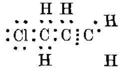
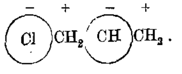
Independent of the considerations discussed below, it seems certain that the introduction of electronegative atoms, such as O, N, Cl, in any position in a molecule increases the power of the whole assemblage to retain electrons. There may still be relative intramolecular differentiations of polarity, but the entire electronegative tone will be raised. An example of this effect is the increased dissociation constant of acids following on the replacement of hydrogen by halogen. The converse proposition holds. The carbon atom is assumed to be nearly neutral in saturated compounds, but its condition in most cases represents a state of compromise, and the arrangement surrounding it is peculiarly susceptible to external influences. Unsaturated carbon atoms may be either negative or positive, according to circumstances.

In the absence of powerful external influences, the following rules appear to afford a trustworthy guide as to the polarity exhibited by carbon atoms in various states of combination. The attachment of carbon to carbon by two electrons induces a very slight constraint on the two octets of which they form a part. This is progressively increased when the number of shared electrons is three and four, and a decided positive polarity of unsaturated carbon is the outcome.

This accounts for the increased mobility of electrons in unsaturated compounds and naturally as a corollary for the selective absorption of light. External influences are, however, seldom absent, and in their presence the function of an unsaturated system, particularly the benzene ring, seems to be analogous to that of a resonator. That is, the external group itself helps to set up a position in which the actual polarity of unsaturated carbon appears to be negative. This is easy to appreciate where a group X affects a group Y via a benzene ring, but what we are now suggesting is that in some cases X affects its own reactivity by the mere fact that it occupies a certain position relative to an unsaturated system.

4. *Induced Polarity in a Chain of Atoms.*

It is possible to represent the majority of carbon compounds so as to have an octet surrounding each carbon, nitrogen, or oxygen atom, but it is quite clear that these cannot all be of equal stability, unless indeed the substance is symmetrically constituted. If in the system, :A:B:C:D:, for some reason internal or external the octet surrounding A becomes stable, this will automatically involve more or less appropriation of the two electrons shared with B, the octet surrounding which is therefore unstable and tends to disintegrate. If, now, another atom C is attached to B, it will have no difficulty in appropriating two further electrons from B, and in doing so may form a stable octet. This again will preclude a fourth member of the chain D from forming a stable octet. In other words, the atoms A, B, C, and D are respectively, −, +, −, +. The case of allyl chloride may be cited as a simple example :

Here the stable octet surrounding the chlorine atom produces an unstable system about the adjacent carbon atom, and therefore the formation of a stable system in the CH group is facilitated and occurs by the aid of two of the electrons held in common with the second unsaturated carbon atom. It is accordingly quite natural that the product of the addition of $\overset{+}{H}\,\overset{-}{Br}$ is trimethylene chlorobromide, $Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.

The case of the influence of positive atoms such as hydrogen and the alkali metals may be considered on precisely similar lines. Such atoms tend to give up an electron and in this way tend to assist the adjacent atom to form a stable octet, and the alternate stable

and unstable systems involving alternate negative and positive polarity are again set up. It must be clearly understood that this view refers only to the mechanism of the alternate effect, and not to the circumstances which induce the "key"-atom to assume its stable octet or to lose an electron. For it is probable that in many molecules the electrons are in a delicate condition of equilibrium very susceptible to external influences, and the character of these may virtually determine the orientation of the alternating stable octets. In the molecules of some substances, however, the activation of any one of the possible "key"-atoms would produce identical results, and in such cases it is certainly feasible to write polar formulæ which will express the behaviour of the compounds in all circumstances. Examples may be found in the structures of *tert.*-butyl alcohol, acetone, acetic acid, acetonitrile, acetoacetic acid, acetonedicarboxylic acid, phloroglucinol in either tautomeric form, orcinol, mesitylene, *s*-xylidine, and many other compounds. One further advantage of the Thomson and Lewis-Langmuir theory in relation to this subject may be noted. Experience has shown that the alternating effect is transmitted but feebly by saturated atoms, whereas it may be discerned at the end of long chains wholly comprised of unsaturated atoms. This is easy to understand in view of the fact that unsaturated atoms share more electrons in common than saturated atoms. There will be a greater mobility of electrons, and the octets, when formed, will have some units at least which are not subject to restraint, a condition which tends to stability.

Although stable octets associated with alternate atoms in a chain represent what is apparently the most common arrangement, it is probable that other structures also occur. For example, in the case of α-diketones such as dimethyl diketone we may write :—

$$\begin{array}{cccc} & \bar{O} & \bar{O} & \\ CH_3 & C & C & CH_3, \\ & + & + & \end{array}$$

and this formulation harmonises with the ready oxidation of the compound by hydrogen peroxide with formation of acetic acid. The quinones are in a similar class, and if these substances are at least partly peroxidic, the explanation may be the tendency to change from the abnormal to the normal (alternate) arrangement of relatively stable octets.

5. *Primary Conjugation.*

The term "primary conjugation" is used to denote a process occurring in the course of a reaction resulting in addition to the

terminal members of an unsaturated system of more than two atoms.

(*a*) *Conjugation of Ethylene Linkings.*—The representation of the active phase and conjugation of butadiene on the partial valency theory is

$$CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \overset{\cdots}{\underset{-}{\cdots}}CH_2{\cdots}CH{\cdots}CH{\cdots}CH_2\overset{\cdots}{\underset{+}{\cdots}}$$

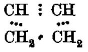
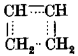
and on the Thomson and Lewis-Langmuir theory as now interpreted

$$\text{(III.)}\quad CH_2\vdots CH{:}CH\vdots CH_2 \qquad \underset{+}{CH_2}\vdots CH{:}CH{:}\underset{-}{\dot{C}H_2}\quad \text{(IV.)}$$

Similarly, the conjugation of three double bonds, supposing such to occur, would be represented thus :—

(V.)

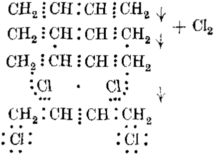
Therefore the notation which has been used in the development of the theory of partial valency acquires a physical meaning if we assume that the symbols $\overline{\overline{\cdots}}$, $\overline{\cdots}$, —, $\cdots$ imply electrons to the number of four, three, two, and one, respectively, held in common by two atoms. Subdivision of a normal valency into more than two partial valencies is accordingly a proceeding of doubtful validity unless one electron can be shared by more than two atoms, or one positive charge on an atomic nucleus by more than two electrons. There is nothing improbable in such an assumption, since the division of the tube or bundle of tubes of force emanating from an electron is already assumed in the hypothesis of shared electrons. Returning to the question of conjugation, we may now consider the mechanism of the additive process. The polarised complexes (IV, V) represent an extreme and highly unstable condition which cannot be the normal state. More stable molecules are the open-chain, non-polarised (III), and the cyclic forms, which latter in the case of butadiene is shown in VI and VII, electronic and partial valency formulæ respectively.

(VI.)   (VII.)

Now either in III or VI the system is probably an oscillating one, the terminal carbon atoms becoming in turn feebly electropositive and electronegative,* and in the absence of a reagent this is the

* In the case of unsymmetrical substances, the considerations discussed in section (4) will determine the polarity of the unsaturated atoms.

extent of the conjugation. We suppose, however, that the reactant takes advantage of these momentary manifestations of polarity and that the process is then carried forward as illustrated below or in some such manner.

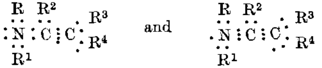


(a.) (b.)

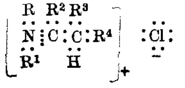
In words, the electrons joining the chlorine atoms one at a time attack a terminal unsaturated carbon atom, driving an electron from the other terminal carbon atom into the electron system surrounding one of the chlorine atoms (*b*). There may, of course, be several intermediate phases, but any such modifications do not affect the principle.

(*b*) *The Ethylene-Nitrogen Conjugated System.*—The partial valency representation of the polarised form of a base,

and the corresponding expressions on the basis of the electronic theory are

 (VIII.)

It is clear the expression VIII denotes a mere alteration in function of the electrons composing the octets, and one of the salt-forming electrons on nitrogen becomes shared with the next carbon, a free electron appearing on the terminal unsaturated carbon atom of the system. If this process occurs a second time, probably as the result of the approach of a reactive molecule capable of dissociation, it may be the carbon which attracts the positive component, and with hydrogen chloride we get the salt (IX).

 (IX.)

The *C*-alkylation of derivatives of aminocrotonic ester and similar substances obviously follows exactly the same course.

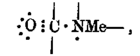
Clearly, therefore, $\geqslant$N (:) is translated by tervalent nitrogen with two salt-forming electrons and $\geqslant$N (⋯) means that one of these has been restrained in its activities by being shared with an adjacent atom. It must be confessed that the power to develop latent valencies exerted by the nitrogen atom to such a remarkable degree is a somewhat mysterious property, the complete explanation of which will probably only be forthcoming when the constitution of the atom as a whole shall have been more precisely elucidated. In the meantime, however, the mechanism of the process is clear enough, and any restraint placed on the free electrons will reduce the salt-forming power of a base.*

6. *Secondary Conjugation.*

This term is applied to those cases where a process analogous to primary conjugation occurs, but does not result in the formation of a product formed by addition at the ends of the conjugated system.

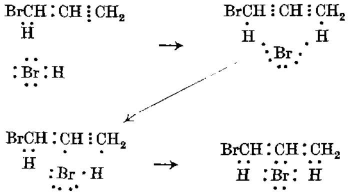
The phenomenon is usually recognised by an orientating effect and is postulated in order to explain the action of a solvent in facilitating certain reactions, and in all those cases where under special conditions different products are obtainable from the same starting-points. Expressed in other words, secondary conjugation is the

* The stability of free electrons in an octet appears to be the greater the larger their number, the extreme case being represented by the chlorine ion. It follows that ammonium salts will be more readily formed and more stable than oxonium salts. Similarly, the more feebly basic character of aromatic as compared with aliphatic amines can be explained by the consideration that the positive unsaturated carbon of the nucleus increases the stability of the nitrogen octet, which accordingly holds its free electrons more firmly and reduces their tendency to attract positive ions. The relative normal instability of the free electrons of the nitrogen atom accounts for the facility with which it enters into conjugated systems. It also seems clear that the non-basic nature of the nitrogen in pyrrole, carbazole, and similar compounds is due to two factors, first, the positive character of the adjacent unsaturated carbon atoms, and, secondly, the existence of only one free electron on the nitrogen atom in the mean phase. It is impossible at present to evaluate the share of these two circumstances in producing the observed results. In cryptopine and protopine, the weakened basic character of the —NMe— group may well be due to the existence of the arrangement

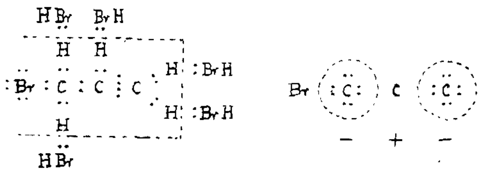


which at the same time explains the loss of reactivity observed in the carbonyl group itself.

result of the activation of a "key"-atom in a molecule on the approach of other molecules either of solvent or reagent. The best examples are to be found in the reactions of aromatic compounds, but in order to illustrate our meaning the addition of hydrobromic acid to allyl bromide may be cited, since this is one of the simplest cases of a reaction proceeding in two directions. The product may be either trimethylene dibromide or propylene dibromide, and, in the former case, a secondary conjugation may be involved, or, on the other hand, it may not, since the normal arrangement in allyl bromide will probably be similar to that given above for allyl chloride and trimethylene dibromide is the natural product. The formation of propylene dibromide is, however, abnormal and the result of the secondary conjugation illustrated below :—



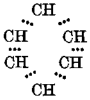
This idea of a loose union between the hydrogen atom and the bromine resulting in orientation of the additive reaction can also be expressed in another way, as shown in the annexed scheme, which represents a process bearing some analogy with Baly's activation of molecules by opening up their fields of force (*Physikal. Z.*, 1913, **14**, 893) :

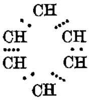


The loosening of the hydrogen atoms by the bromine produces the result illustrated alongside on the stability of the octets. It should be noted that the effect of the centrally situated hydrogen atom opposes that of the remaining four.

7. *Aromatic Nuclei.*

(*a*) *Homocyclic Types.*—In discussing the subject of conjugation, we have tacitly assumed that three electrons shared by two atoms is a relatively stable configuration, and the electronic formula for benzene corresponding with the cyclic conjugated expression with six sesquivalencies (X) is shown in XI.

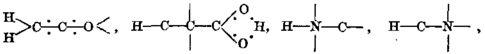


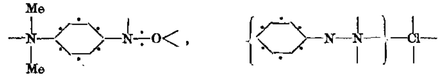


(X.) (XI.) * (XII.)

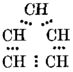
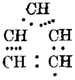
The relation of XI to the Kekulé formula XII is seen to be a remarkably close one and to involve the movements of electrons, not from atom to atom, but merely to new positions in three octets. If, therefore, the benzene molecule is in fact, as many chemists have assumed, subject to vibrations and in a dynamic condition, a relatively insignificant rearrangement is required in order to pass from one Kekulé formula to the other. This consideration suffices to explain the non-existence of pentamethine (XIII) or any of its derivatives, since this compound could scarcely survive the passage into the phase XIV without undergoing polymerisation to a substance such as XV.

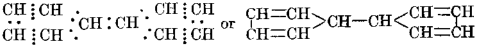
* We venture to suggest that the following conventional notation is simple and convenient. Represent a single electron by a dot (and if held in common by two atoms its position will indicate this), two electrons by an ordinary bond. Varied structures are readily expressed in this manner; thus our view of the electronic constitutions of keten, propiolic acid, carbylamine, formonitrile, nitrosodimethylaniline, and benzenediazonium chloride are the following :—





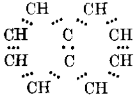
The formula chosen for the carboxyl group is identical with the expression, H, recommended by Hantzsch and by Lapworth.

(XIII.)   (XIV.)

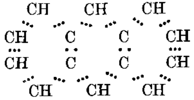


(XV.)

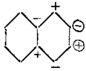
The most stable or mean phases of naphthalene and anthracene are shown in (XVI) and (XVII) respectively,



(XVI.)



(XVII.)

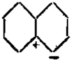


(XVIII.)

and it is interesting to observe that whatever arrangement of octets is chosen it is impossible that both the central quaternary atoms in naphthalene or more than two such atoms in anthracene can he surrounded by stable electron systems. One of these atoms in naphthalene and two of them in anthracene * must therefore be intensely positive, and, in accordance with the considerations advanced in (4) above, this explains very satisfactorily the reactive nature of the α-position in naphthalene and the 9- and 10-positions in anthracene. Taking the case of naphthalene, we have the

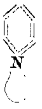
* As a matter of fact, the environment of the central carbon atoms of the naphthalene and anthracene nuclei tends to make them all positive, in accordance with the views expressed on p. 430 in connexion with the effect of various types of combination on the polarity of carbon atoms. The suggestion put forward in the text implies that in the case of one of these atoms in naphthalene the tendency to form a system of alternate stable and unstable octets overbears its natural positive character. This again is bound up with the nature of the mechanism of substitution in aromatic compounds, the theory adopted being correlated with the additive hypothesis of such reactions. In considering the chemistry of polynuclear compounds generally, it should, however, be remembered that the carbon atoms common to two rings have a tendency to evince positive polar character.

The possibility must not be overlooked that the types represented by H_2, Br_2, and $HO{\cdot}NO_2$ may react most easily with different phases of an unsaturated molecule. Thus the formation of 1 : 4-dihydronaphthalene appears natural if regarded as the result of a symmetrical addition of hydrogen to naphthalene in the phase

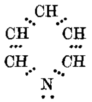
 .

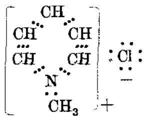
condition shown in XVIII, and addition occurs to the 1 : 4-positions preferentially as being the nearest to the source of the disturbance leading in non-reversible substitutions to the replacement of hydrogen in the α-position. In reversible substitutions, for example, sulphonation, the weaker induced activity of the β-positions can come into operation.

(*b*) *Heterocyclic Types.*—The heterocyclic aromatic substances which are typical of all others are pyridine and pyrrole, and to these the cyclic conjugated formulæ XIX and XX have been assigned by one of us in order to express the basic properties of the former substance and the non-basic properties of the latter.

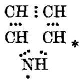

(XIX.)

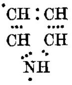
(XX.)


(XXI.)


(XXII.)

The case of pyridine presents no unusual feature, and the formulæ XXI and XXII can be assigned to the base and its methochloride. Pyrrole, however, appears to have a peculiar electronic configuration, shown in XXIII, which is an exact rendering of XX in accordance with the principles suggested above in discussing the ethylene–

(XXIII.)



(XXIV.)

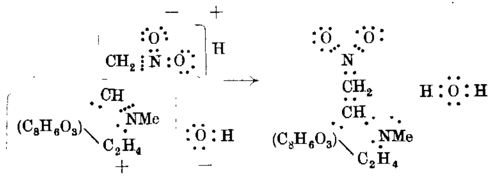
nitrogen conjugated system. The peculiarity is the existence of an unrestrained electron, denoted by an asterisk, on the α-carbon atom. The properties of pyrrole are in complete harmony with this interpretation.

The occasional reactivity of the β-position is due to incomplete conjugation resulting in the phase XXIV, and on the basis of these views it is readily explicable that it is the α-position which is the most reactive in pyrrole and the β-position in indole.

8. *Mechanism of Reactions.*

The mechanism of reactions appears in many cases notably simplified by a reference to the electronic basis. As a single example we take the condensation of a pseudo-acid (nitromethane) in its *aci*-form with a pseudo-base (cotarnine) in its ammonium hydroxide

form, leading to a product (anhydrocotarninenitromethane), in which both acid and base automatically revert to the pseudo-condition.



The only rearrangements of electrons involved in this process are in the octets themselves and in no case does an electron leave the octet of which it forms a part.

Finally, it may be noted that intramolecular rearrangements are equally readily represented, and that, for example, the generalised form (R. Robinson, *Mem. Manchester Phil. Soc.*, 1920, **64**, iv, 7) of the pinacone–pinacolin and Wagner transformations is capable of literal translation into the electronic expressions if to the partial valencies is given the meaning suggested on p. 433.

In the foregoing, an attempt has been made to show that the Thomson and Lewis-Langmuir theory of valency and electron configuration furnishes a satisfactory physical basis for certain modern hypotheses of organic chemistry, and if this attempt has been at all successful the matter is certainly not lacking in that special interest which accrues when ideas derived from different points of view are found to be compatible.

A very brief statement of these views was sent to Professor A. Lapworth, F.R.S., in December, 1921, and he at once replied that he had drawn similar conclusions which were embodied in a general form in a paper which he had submitted to the Society a short time before the receipt of the letter. The present communication is the outcome of his generous suggestion that we should submit our manuscript before having an opportunity to consult his own publication.

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Edinburgh.

[*Received, January 11th, 1922.*]

LII.—*The Amphoteric Character of Stannic Hydroxide and its bearing on the Isomerism of the Stannic Acids.*

By GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD.

ONE of the authors has, in previous papers (T., 1908, **93**, 411; 1910, **97**, 878; 1916, **109**, 164), described investigations the object of which was the comparison of the basic and acidic affinities of various metallic hydroxides. It appeared to the authors that it would be of interest to make a study of stannic hydroxide from the same point of view, although it was fully anticipated that the investigation of this substance would present difficulties much greater than had been experienced in the earlier experiments. It may be said at once that this expectation was fully realised. It was found possible to determine approximately the degree of hydrolysis of solutions of stannic chloride by the methyl acetate catalysis method and to measure the amount of hydrolysis in solutions of potassium stannate by their influence on the decomposition of nitrosotriacetonamine; the results obtained are given in the experimental part of this paper. Of the two series of experiments, those with the stannate solutions are probably the more dependable; in some of the stannic chloride experiments precipitation of stannic hydroxide took place, and this change in the system makes it impossible to regard the results otherwise than as of an approximate character. The values obtained for the degree of hydrolysis of the two salts were sufficient to confirm the view previously expressed by various investigators that stannic hydroxide is a much stronger acid than it is a base, thus justifying the name of stannic acid commonly applied to it.

Among the methods of investigation employed on former occasions the determination of the solubility of the metallic hydroxide in solutions of hydrochloric acid and of sodium hydroxide was found to be of value. When this method was applied to stannic hydroxide, however, it was found impossible to attain equilibrium in the great majority of the mixtures even after prolonged contact. The behaviour of stannic hydroxide under the conditions specified will be fully dealt with in a further communication, but it was of such a character as made it essential to consider fully the subject of the isomerism of the stannic acids. This consideration has led the authors to form certain opinions with regard to the underlying cause which is responsible for the change of the so-called α-stannic acid into β-stannic acid. Before stating these opinions it is necessary

to review briefly the more important of the very numerous contributions relating to the isomerism of the stannic acids.

A study of the literature reveals two main lines of opinion concerning the stannic acids. The one is the view introduced by Frémy (*Ann. chim. phys.*, 1848, [iii], **23**, 393) and supported by Rose (*Pogg. Ann.*, 1848, **75**, 1), Engel (*Compt. rend.*, 1897, **124**, 765; 1897, **125**, 464, 651, 709), and Kleinschmidt (*Monatsh.*, 1918, **39**, 149) to the effect that two distinct substances of definite composition are capable of existence; Engel, in fact, considered a third isomeride, parastannic acid, to be capable of existence, but doubt was thrown on this by Kleinschmidt. In opposition to this view we have the theory which seeks to explain the behaviour of the different modifications of stannic acid from the point of view of colloid chemistry. In support of this opinion it is pointed out that some of the compounds which have been described as of constant composition may, as a matter of fact, show a very considerahle variation in composition. Thus Ordway (*Silliman's American Journal of Science*, 1865, p. 173) showed that the meta-stannates might have a composition shown by formulæ such as $Na_2O,3SnO_2$; $Na_2O,5SnO_2$; $Na_2O,7SnO_2$, etc. Vignon (*Compt. rend.*, 1889, **108**, 1049), from measurements of the heat of reaction between alkali and the various modifications of stannic acid, concluded that a series of polymerisations takes place during the conversion of the α- into the β-variety, giving rise to a product of smaller basicity. The investigation of the dehydration and rehydration of stannic acid gels by van Bemmelen ("Die Absorption," pp. 54 *et seq.*; 393 *et seq.*) failed to yield any evidence of the existence of definite hydrates of stannic oxide; he considered both the stannic acids to be colloids and the so-called meta-stannates to be adsorption compounds. These views were somewhat extended by Biron (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 933; 1905, **37**, 963, 994, 1036), who considered that by the condensation of α-stannic acid an uninterrupted series of β-acids could be obtained, but neither he nor van Bemmelen expressed any opinion as to the cause of the α-β-change. Wagner (*Monatsh.*, 1913, **34**, 95, 931; *Kolloid Z.*, 1914, **14**, 149) directed attention to the decrease of surface which takes place when a gel gradually separates out from a solution and showed that this factor is of importance in connexion with the slow hydrolysis of solutions of stannic chloride. Amongst the most important contributions to the colloidal explanation of the isomerism of the stannic acids those made by Mecklenburgh are particularly worthy of note. In a series of papers (*Z. anorg. Chem.*, 1909, **64**, 368; 1912, **74**, 207; 1914, **84**, 121) he correlated the data in a very convincing manner and attributed the different behaviour shown by the modifications of stannic acid to a difference in the size

of their primary particles; the modifications having the most highly developed β-character were regarded as having the largest primary particles. This hypothesis has been accepted by Zsigmondy and his co-workers, Heinz and Franz; the latter (*Diss.*, Göttingen, **1913**) expressed the view that the primary particles are of amicronic dimensions and that in sol systems there is a gradual transition from the molecular state to primary particles and onwards, by complex formation, to secondary particles.

It will have been noticed that in these various expressions of opinion, whilst the properties of a particular preparation of stannic acid are considered to be dependent on the size of the particles of the substance, there is no reference to causes which may have a controlling influence on the magnitude of the primary particles. Mecklenburgh certainly refers to the influence of physical conditions, such as the temperature of preparation, on the nature of the product obtained, but it does not follow from this that size of the particles is determined either wholly or primarily by the operation of physical forces. Tian (*Compt. rend.*, 1921, **172**, 1402) has suggested that the union of colloidal particles, resulting in a decrease in the degree of dispersion, is due to the operation of capillary forces. The authors, however, have formed the opinion that the change in the size of the particles, and therefore the decision regarding the properties which shall be possessed by the resulting product, is due to chemical action; the possibility of such chemical action is to be traced, in the case of the stannic acids, to the amphoteric character of stannic hydroxide. The authors desire to point out, however, that this theory of the cause underlying the α-β-change is applicable not only to the stannic acids, but also to the analogous compounds of titanium, zirconium, and other elements; the isomerism of the tungstic acids is probably explainable on the same hypothesis. It is surely something *more than a mere coincidence that the elements which form* so-called isomeric acids such as those at present under consideration should all form hydroxides of a more or less well-defined amphoteric character.

Illustrating this theory by reference to stannic acid, this substance, at the moment of its formation, doubtless exists as the ortho-compound, $Sn(OH)_4$. This is capable of ionisation both as an acid and as a base, and it is possible therefore to conceive of a process akin to salt formation taking place, either in the same molecule, which would yield a compound such as $SnO(OH)_2$, or between two molecules, giving a product like $(OH)_3Sn{\cdot}O{\cdot}Sn(OH)_3$. These products would, however, still be capable of ionisation, although probably to a less degree than the original molecules of $Sn(OH)_4$; the process of salt formation would therefore continue, thus leading

to the production of condensation products of gradually increasing complexity. If the view of Bellucci and Parravano (*Z. anorg. Chem.*, 1905, **45**, 142) with respect to the constitution of stannic acid be accepted, it is probable that a portion of the stannic hydroxide would, soon after its formation, unite with water to yield a product having the formula $H_2Sn(OH)_6$ and that salt formation would then take place between this substance and some of the unchanged stannic hydroxide; this process of condensation would then continue, as previously indicated, to give products of yet greater complexity. The greater the extent to which this union between molecules takes place, the smaller will become the surface of the product in comparison with the total surface of the original molecules, and the smaller will be the tendency of the substance to unite with others, owing to so much of the affinity of the original molecules having been satisfied. This hypothesis, therefore, gives an adequate explanation of why different preparations of stannic acid may be made up of particles of varying size and of why the particles of larger dimensions should be possessed of smaller chemical activity and a relatively smaller capacity of adsorption. It also naturally follows that any physical condition which promotes chemical action will tend to favour this process of salt formation or condensation, and that the product will be possessed therefore of a more pronounced β-character the higher the temperature at which it is prepared. The difference in the heats of neutralisation of different modifications of stannic acid as observed by Vignon (*loc. cit.*) is obviously easily accounted for on the theory which has been advanced. Various other phenomena, such as differences in the ease of peptisation of different specimens of stannic acid, the slow hydrolysis of stannic salts, and specific cases of adsorption, will be discussed in detail in future communications. It may be here mentioned, however, that the experimental results relating to these subjects which are recorded in the literature, as well as those which have been obtained by the authors, are in agreement with the requirements of the theory. It may also be of interest to state that experiments are at present in progress in these laboratories upon titanic and zirconium hydroxides, whilst it is hoped soon to commence work on tungstic acid; the results so far obtained in these other investigations are in harmony with the general theory which has been advanced.

Whilst, on general grounds, the authors are of the opinion that the colloidal theory of the isomerism of the stannic acids gives a better general explanation of the facts than does the alternative view of the existence of definite compounds, it is worthy of note that the hypothesis which has been advanced in explanation of the cause

of the α-β-change is not absolutely opposed to the existence of definite compounds. Whilst the conception which has been advanced is one involving a continuous series of condensation products of gradually increasing complexity, it is certainly within the bounds of possibility that under certain conditions all the condensed molecules formed should be possessed of the same composition, in which case the condensation product will appear to be a definite compound to which a particular formula may be ascribed.

In concluding this portion of the present communication, it may be observed that Pauli, in a paper on the structure of colloids (Faraday Society, Discussion on Colloids, October, 1920, published 1921), has also expressed the view that many sols of metallic componnds contain complex molecules due to the union of, for example, some of the simple molecules of the original substance with molecules formed by the hydrolysis of the original compound. Whilst this is of interest as being an attempt to trace the difference in the properties of colloids to the operation of chemical action, it does not appear to be so definite a statement as that advaneed by the authors, inasmuch as no particular cause appears to be given as to why this complex formation should take place, nor is the mode of union of the constituent simple molecules suggested.

EXPERIMENTAL.

The Degree of Hydrolysis of Aqueous Solutions of Stannic Chloride, as indicated by the Methyl Acetate Catalysis Method.

The solutions used were prepared by adding about 2·9 c.c. of stannic chloride to 50 c.c. of distilled water in a stoppered bottle, rapidly shaking to dissolve the substance, and then making up the volume to 500 c.c. The concentration of the resulting solution was then determined by analysis, the chlorine being estimated by Volhard's method and the tin by precipitating as sulphide and then converting into oxide. The results of these determinations were in complete agreement, a particular solution giving chlorine concentration 0·1967*N* and tin concentration 0·1964*N*.

One hundred c.c. of such a solution contained in a well-corked flask were raised to 25° in the thermostat; after attaining the temperature of the bath, 4 c.c. of freshly distilled methyl acetate were added, the whole was well shaken, and a portion of 4 c.c. removed and titrated with barium hydroxide solution of approximately decinormal concentration; at suitable intervals further portions of 4 c.c. were removed and titrated; to ensure greater accuracy all titrations were conducted in duplicate, two portions of solution being removed from the flask immediately after each

other. In the preliminary series of experiments, the velocity constant of the action was compared with that obtained from a similar experiment in which a solution of hydrochloric acid of the same chlorine concentration as the stannic chloride solution was allowed to react with methyl acetate; the approximate degree of hydrolysis having thus been determined, a more exact measure was then made, using a comparison solution which contained hydrochloric acid and potassium chloride, the total chlorine concentration being the same as before and the concentration of free acid the quantity indicated by the preliminary determination.

As mentioned in the earlier part of the paper, a precipitate was gradually deposited from some of the solutions. The formation of this precipitate did not appear to have any disturbing influence on the reaction, the velocity constant remaining practically unchanged even although a considerable change in the character of the solution took place; this is illustrated by the following values obtained for the velocity constant with a solution which was clear at the commencement of the experiment, but was exceedingly turbid when the last values were obtained.

Time in mins.	Appearance of liquid.	$k \times 100$.	Time in mins.	Appearance of liquid.	$k \times 100$.
0	Clear	—	922	—	0·115
652	Opalescent	0·113	1011	Heavy turbidity	0·117
710	—	0·113	1117	—	0·115
822	—	0·115	1257	—	0·115
868	—	0·114			

The following results were obtained with a 0·197*N*-solution which had been kept for three days after preparation; a precipitate had formed in the solution.

Time.	Titre.	$a-x$.	$k \times 100$.	Time.	Titre.	$a-x$.	$k \times 100$.
0	21·68	41·74 (=a)	—	1070	52·81	10·51	0·128(0)
696	46·74	16·68	0·131(8)	1231	54·98	8·44	0·130(0)
750	48·00	15·42	0·131(2)	1370	56·37	7·05	0·129(0)
881	50·10	13·32	0·129(6)	∞	63·42		—
958	51·45	11·97	0·130(5)				
						Mean	0·1300

Results obtained with the comparison solution containing hydrochloric acid and potassium chloride; total chlorine concentration 0·198*N*, concentration of acid 0·173*N*.

Time.	Titre.	$a-x$.	$k \times 100$.	Time.	Titre.	$a-x$.	$k \times 100$.
0	19·10	42·16 (=a)		1068	49·78	11·48	0·121(8)
704	43·64	17·62	0·123(9)	1216	52·54	8·72	0·129(6)
761	44·58	16·68	0·121(8)	1374	53·38	7·88	0·122(0)
826	45·43	15·83	0·118(6)	2232	58·25	3·01	0·118(2)
886	46·86	14·40	0·121(3)	∞	61·26		—
963	48·05	13·21	0·120(2)				
						Mean	0·121(9), *i. e.* 0·122

From the two velocity constants given, it is obvious that the free acid in a 0·197*N*-solution of stannic chloride has a concentration of 0·184*N*. It is impossible to state with certainty the mode of hydrolysis of stannic chloride, but from the large amount of free acid present it appears very probable that the reaction takes place in accordance with the equation

$$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl.$$

Assuming the action to be correctly represented by the above equation, the figures given above indicate that a 0·197*N*-solution of stannic chloride is hydrolysed to the extent of about 94 per cent. at 25°.

Similar experiments were carried out with a more concentrated solution of stannic chloride, the actual concentration being 0·396*N*. In this case no precipitation of stannic hydroxide took place, the substance all remaining, presumably, in the colloidal condition. The comparison of the velocity constant with that given by the comparison solution (a 0·397*N*-solution of hydrochloric acid) indicated that the concentration of free acid was 0·286*N*, corresponding with a degree of hydrolysis of 72 per cent.

Investigation of the Hydrolysis of Potassium Stannate.

The material used in these experiments was prepared by the method described by Marignac (*Annales des Mines*, 1859, [v], **15**, 277). Thirty grams of α-stannic acid (prepared by the action of calcium carbonate on a solution of stannic chloride, followed by thorough washing and drying in air) were fused with 80 grams of potassium hydroxide, and the cold product was extracted with hot water and filtered. The filtered solution was evaporated until saturated, and was then placed in a vacuum over concentrated sulphuric acid, as recommended by Musculus (*Ann. chim. phys.*, 1868, [iv], **13**, 95); the acid was subsequently replaced by sodium hydroxide. By this means small, clear crystals were obtained which were filtered off, rapidly washed once with distilled water, then several times with alcohol, and finally with ether. When dry to the touch, the product was dissolved in distilled water and the solution analysed; the alkali was estimated by titration with hydrochloric acid, using methyl-orange as indicator, and the tin by reduction with aluminium and hydrochloric acid and subsequent titration with iodine. The results showed that the potassium and tin were present in the atomic ratio of 2 : 1, the concentration of the solution being 0·231*N*.

It may be mentioned that several attempts were made to purify

the potassium stannate by washing several times with water and then with alcohol until the washings showed no alkaline reaction, this being the method advocated by Bellucci and Parravano (*loc. cit.*); the substance prepared in this way was not completely soluble in water and contained less than the theoretical quantity of alkali.

The amount of hydrolysis in the solution prepared as above was determined by the method based on the decomposition of nitrosotriacetonamine (Clibbens and Francis, T., 1912, **101**, 2358; Francis and Geake, T., 1913, **103**, 1722); the authors have pleasure in expressing their thanks to Professor Francis for a sample of the nitroso-compound which he kindly supplied to them. The determinations were made at 25°, the solution of nitrosotriacetonamine being contained in a wide-necked flask fitted with a rotary stirrer provided with a mercury seal, and having, also, a capillary tube leading to the nitrometer in which the evolved nitrogen was collected and measured; the stannate solution was separately warmed to the temperature of the bath and was then run into the flask through a tap funnel. It appeared possible that this dilution of the stannate solution might be attended by a slow alteration of the amount of hydrolysis, but preliminary experiments showed this to be unlikely, the velocity constant of the reaction being of practically unchanged value throughout the whole course of the reaction.

0·13 Gram of nitrosotriacetonamine was dissolved in 20 c.c. of water and 25 c.c. of 0·231 *N*-potassium stannate solution added; after mixing, the concentration of the stannate solution was 0·128*N*. The solution was slightly opalescent and remained so throughout the experiment.

Time of reading in minutes.	Reading of nitrometer.	$V_\infty - V_t$.	$k = \frac{1}{t}\log_e \frac{V_\infty - V_0}{V_\infty - V_t}$.	Time of reading in minutes.	Reading of nitrometer.	$V_\infty - V_t$.	$k = \frac{1}{t}\log_e \frac{V_\infty - V_0}{V_\infty - V_t}$.
0	3·15	15·15 $(= V_\infty - V_0)$		47	11·80	6·50	0·0180
12	6·05	12·25	0·0177	50	12·15	6·15	0·0180
15	6·60	11·70	0·0172	55	12·65	5·65	0·0179
19	7·45	10·85	0·0175	61	13·20	5·10	0·0178
22	8·05	10·25	0·0177	65	13·50	4·80	0·0177
24	8·40	9·90	0·0177	72	14·05	4·25	0·0177
27	8·90	9·40	0·0177	82	14·65	3·65	0·0173
30	9·40	8·90	0·0177	87	15·05	3·25	0·0177
33	9·85	8·45	0·0177	94	15·40	2·90	0·0176
36	10·40	7·90	0·0181	100	15·67	2·63	0·0175
39	10·80	7·50	0·0180	∞	18·30	0·00	
42	11·20	7·10	0·0180				

Mean 0·0177

Decomposition of Nitrosotriacetonamine in Presence of Comparison Solution.

The comparison solution was prepared to contain approximately the same concentration of potassium hydroxide as preliminary experiments had indicated to be present in the stannate solution, potassium sulphate being added so as to make the concentration of potassium the same in the two solutions. In the experiment in question, the concentration of potassium hydroxide, after mixing with the solution of the nitroso-compound, was 0·018*N*, the total potassium concentration being 0·129*N*.

Time of reading.	Nitrometer reading.	$V_\infty - V_t$.	*k*.	Time of reading.	Nitrometer reading.	$V_\infty - V_t$.	*k*.
0	2·00	14·75 ($V_\infty - V_0$)		34	8·90	7·85	0·0185
3	2·85	13·90	0·0188	40	9·73	7·02	0·0184
6	3·65	13·10	0·0193	46	10·50	6·15	0·0189
9	4·43	12·32	0·0197	50	11·00	5·75	0·0188
12	5·03	11·72	0·0189	55	11·50	5·25	0·0187
15	5·60	11·15	0·0186	60	12·00	4·75	0·0184
18	6·20	10·55	0·0185	65	12·45	4·30	0·0189
21	6·75	10·00	0·0184	72	13·05	3·70	0·0192
24	7·30	9·45	0·0182	75	13·27	3·48	0·0192
27	7·80	8·95	0·0184	80	13·60	3·15	0·0193
30	8·30	8·45	0·0185	∞	16·75	0·00	
						Mean	0·0188

From a comparison of the velocity constants, it is obvious that the concentration of free alkali in the solution of the stannate must be 0·017*N*. Assuming that the hydrolysis of the salt takes place in the manner represented in the following equation

$$K_2Sn(OH)_6 + 2H_2O \rightleftharpoons H_2Sn(OH)_6 + 2KOH,$$

the amount of free alkali present is equivalent to a degree of hydrolysis of 13 per cent.

The fact that a 0·128*N*-solution of potassium stannate is hydrolysed only to the extent of 13 per cent., whereas a somewhat more concentrated solution (0·197*N*) of stannic chloride is hydrolysed to the extent of 94 per cent. shows conclusively that stannic hydroxide is considerably stronger as an acid than as a base.

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LIII.—*Complex Metallic Ammines. Part VII. Conductivities of Diethylenediaminecobaltic Bromides.*

By JAMES COOPER DUFF.

WERNER (*Annalen*, 1911, **386**, 81) described the preparation and properties of *cis*-sulphitodiethylenediaminecobaltic chloride from *trans*-dichlorodiethylenediaminecobaltic chloride and sodium sulphite. He obtained the salt in dark brown crystals. All the other known *cis*-salts of this type, containing a dibasic radicle, are red or purple-red in colour. As these have the acid radicle linked to cobalt through oxygen, Werner explained that the sulphito-chloride was brown because the sulphite group was linked up with the cobalt atom by means of a sulphur valency, and he therefore wrote the formula I.

$$\text{(I.)}\quad \left[{\overset{\displaystyle O}{\underset{\displaystyle O_2S}{}}}{>}Co\,en_2\right]Cl \qquad\qquad \left[O_2S{<}{S \atop O}{>}Co\,en_2\right]Br\quad\text{(II.)}$$

To obtain more conclusive evidence that sulphur linked directly to cobalt in the complex causes the salts to have a brown colour, attempts were made to obtain the thiosulphato-bromide (II), in which sulphur must be directly linked to cobalt. Following Werner's method for sulphito-chloride, the reaction between sodium thiosulphate and *trans*-dicblorodiethylenediaminecobaltic chloride was investigated. Cobalt sulphide was found to separate as evaporation proceeded. Apparently a salt of the formula III

$$\text{(III.)}\quad \left[{H_2O \atop H_2O}Co\,en_2\right]{Cl \atop S_2O_3} \qquad\qquad \left[O_2S{<}{O \atop O}{>}Co\,en_2\right]Br\quad\text{(IV.)}$$

was first formed, and instead of the thiosulpbate radicle replacing the two aquo-groups in the usual way, the complex decomposed and cobalt sulphide formed. Tbe desired bromide was, however, obtained from the carbonato-bromide and harium thiosulphate (see experimental part). This method is exceptional, since there is apparently no intermediate formation of a diaquo-salt, as is the case for the bromides described in the preceding parts of this series. The thiosulphato-bromide obtained was dark brown in colour. For comparison, the sulphato-bromide IV was prepared in the usual way from sulphuric acid and the carbonato-bromide. It was obtained in dark red crystals similar to those of the carbonato-bromide. In the sulphato-bromide the sulphur is not directly

linked to cobalt. The results indicate that sulphur linked directly to cobalt causes the brown colour of the sulphito- and thiosulphato-salts.

Werner and Miolati (*Z. physikal. Chem.*, 1893, **12**, 34; 1894, **14**, 506) measured the electrical conductivities of solutions of complex ammonia salts of platinum, cobalt, and chromium, and obtained results which readily distinguished between salts showing one, two, or three ions in addition to the complex ion. Those salts with one free ion gave values for the molecular conductivity at 25° ranging from 96·7 to 108·5. Salts yielding two free ions in addition to the complex ion gave values between 234·4 and 267·6, and those salts which yielded three free ions in addition to the complex gave values from 383·8 to 426·9.

In addition to the three salts described above, a series of bromides of the type [ACo en_2]Br, in which A is the radicle of a dibasic organic acid, has been described in the last three parts of this series (T., 1920, **117**, 1071; 1921, **119**, 385, 1982). These have all been prepared from the same compound, *cis*-carbonato-diethylenediaminecobaltic bromide, by very similar methods, and for this reason the similarity in their structure may be more safely assumed. Their molecular conductivities have been measured, and the results given below agree with those found by Werner and Miolati (*loc. cit.*) for salts yielding one free ion in addition to the complex ion.

The molecular weights of the bromides used vary from 319 for the carbonato-bromide to 533 for the dibromosuccinato-bromide. The results obtained indicate that with increasing weight in the complex ion there is a greater tendency for this ion to hydrolyse in dilute solution. Where hydrolysis was avoided, the size of the complex ion seemed to have no influence on the final figures obtained. From the results, it will be seen that for eight bromides the values of μ are between 103·5 and 108·3.

The presence of a sulphonic group in the complex in place of the carboxyl group seems also to lead to greater hydrolysis of the complex in dilute solution. This applies to the aliphatic sulphonic derivatives. The only aromatic sulphonic derivative, *o*-sulphobenzoic acid, in the complex, gives results which show less hydrolysis than is the case with the corresponding phthalato-bromide. The sulphato-radicle, as in the sulphato-bromide, behaves like the sulphonic radicle in its tendency to cause hydrolysis of the complex in dilute solution. Where, however, a sulphur atom is directly linked to the cobalt atom in the complex, there is evidence of greater stability in the complex. This is noticed on comparing the results for sulphato- and thiosulphato-bromides.

Considering the results in relation to the size of the ring system produced by the dicarboxylic acid and the cobalt, the figures show that where there are not more than six atoms in the ring the complex resists hydrolysis at 25°. The only representatives of a seven-membered ring system, produced from dicarboxylic acids, which appreciably resist hydrolysis, are the succinato- and phthalato-bromides. Maleato-, mesotartrato-, and dibromosuccinato-bromides give results which indicate hydrolysis increasing in the order named.

The case of the methionato-bromide is of interest. This was one of the most difficult bromides to prepare (T., 1920, **117**, 1073). The electrical conductivity results show that hydrolysis occurs in the complex very readily in solution. This explains why the methionato-methionate (*loc. cit.*), although almost insoluble in cold water, was only obtained in quantity during the preparation by evaporation of the solution to low bulk. Also this salt is very soluble in cold dilute ammonia solution, and yet cannot be reprecipitated from this on acidifying. This is now explained by the hydrolysis of the complex which occurs in the ammonia solution.

Experimental.

cis-*Sulphatodiethylenediaminecobaltic bromide*, $[SO_4Co\,en_2]Br,H_2O$, was obtained in dark red crystals by slowly adding the equivalent amount of *N*-sulphuric acid (31·3 c.c.) to a hot solution of carbonatodiethylenediaminecobaltic bromide (5 grams) in 100 c.c. of water, and evaporating on the water-bath to low bulk (Found: Co = 15·61; Br = 21·32; SO_4 = 25·68; H_2O = 5·01. $C_4H_{16}O_4N_4BrSCo,H_2O$ requires Co = 15·81; Br = 21·42; SO_4 = 25·75; H_2O = 4·83 per cent.).

The crystals slowly become anhydrous on exposure to air. A solution in water gives no precipitate with barium chloride until after heating, thus proving that the sulphato-radicle is entirely in the complex.

cis-*Sulphitodiethylenediaminecobaltic bromide*, $[SO_3Co\,en_2]Br,3H_2O$, was obtained in golden-brown needles after adding slowly a 5 per cent. sulphurous acid solution to a hot solution of 5 grams of the carbonato-bromide in 100 c.c. of water. Five per cent. excess of the equivalent amount of sulphurous acid was used, and the resulting brown solution was evaporated to low bulk on the water-bath (Found: Co = 14·85; Br = 20·10; SO_3 = 20·28; H_2O = 13·81. $C_4H_{16}O_3N_4BrSCo,3H_2O$ requires Co = 15·01; Br = 20·33; SO_3 =

20·36; H_2O = 13·74 per cent.). A fresh solution of the bromide gives no precipitate with barium chloride until the solution is heated, when barium sulphite slowly separates. In other reactions, it resembles the chloride described by Werner (*loc. cit.*).

cis-*Thiosulphatodiethylenediaminecobaltic bromide*,

$$[S_2O_3Co\ en_2]Br,3H_2O,$$

was obtained in dark brown, irregular plates on adding barium thiosulphate, BaS_2O_3,H_2O (4·18 grams), to a hot solution of the carbonato-bromide (5 grams) in 100 c.c. of water, and heating in boiling water for one hour. After filtering from the barium carbonate which separated, the solution was evaporated to low bulk at a temperature under 50°. Evaporation at higher temperatures causes the separation of cobalt sulphide. The salt requires recrystallising from water (Found: Co = 13·93; Br = 18·60; S = 15·21; H_2O = 12·39. $C_4H_{16}O_3N_4BrS_2Co,3H_2O$ requires Co = 13·88; Br = 18·80; S = 15·09; H_2O = 12·71 per cent.).

The thiosulphato-group is entirely in the complex, since a freshly-prepared solution shaken with freshly-precipitated moist silver oxide gives a hydroxide from which all bromine has been removed, but which contains the thiosulphato-radicle, its presence being indicated by warming either with dilute sulphuric acid or with silver nitrate solution.

Molecular Conductivities.

All the electrical conductivities were measured in the same Kohlrausch cell, the cylindrical form narrowed at the foot being used. The electrodes were freshly platinised, and the cell constant was found by means of 0·02*N*-potassium chloride solution. A Wheatstone bridge with 100 cm. scale was used together with an induction coil and telephone for measuring the resistance of each solution. A current of four volts was obtained from dry cells. The measurements were all made at 25° in a thermostat, and all solutions were prepared at or under 25° to avoid the possibility of increased hydrolysis of the complex at higher temperatures.

The numbers in the first column of the following table indicate the bromides in the following order:—(1) Carbonato-, (2) sulphato-, (3) snlphito-, (4) thiosulphato-, (5) oxalato-, (6) malonato-, (7) sulphoacetato-, (8) benzylsulphoacetato-, (9) methionato-, (10) succinato-, (11) maleato-, (12) mesotartrato-, (13) dibromosuccinato-, (14) phthalato-, and (15) *o*-sulphobenzoato-diethylenediaminecobaltic bromides.

	$v =$ 32	64	128	256	512	1024
1.	$\mu =$ 90·46	96·85	101·4	103·5	105·4	106·1
2.	90·4	98·56	106·9	114·0	119·7	125·2 107·4*
3.	89·32	99·24	108·1	115·1	122·8	127·6 120·4*
4.	83·18	90·65	96·40	104·1 99·97*	113·0 101·6*	118·5 103·5*
5.	86·62	94·12	100·1	103·9	107·6 105·6*	107·7 106·8*
6.	85·96	91·62	98·35	100·7	103·2	106·7 105·6*
7.	89·32	96·25	103·3	106·5	112·6 105·3*	115·4 106·8*
8.	85·53	94·50	103·5	111·8	116·9 101·9*	124·4 103·5*
9.	112·7	182·3	209·9	242·2	281·5	317·6 269·9*
10.	71·39	78·77	86·48	94·84	103·6	107·2 106·8*
11.	77·13	87·84	99·56	103·9	119·8 115·5*	126·6 118·2*
12.	95·76	121·6	145·3	169·8	197·4	214·8 193·6*
13.	130·8	178·6	202·4	230·8	256·9	274·5 217·1*
14.	76·00	85·23	95·23	101·6 94·14*	113·4 105·2*	121·0 108·3*
15.	70·94	80·61	89·04	95·85	106·4	108·8 105·6*

* These figures were obtained by using freshly made solutions.

Addendum.

The only bromide in the list for which conductivity values have been previously published is the oxalato-bromide (No. 5). For the purpose of the preceding measurements it was prepared by Price and Brazier's method (T., 1915, **107**, 1376). The salt obtained had the formula $[C_2O_4Co\,en_2]Br,H_2O$. Werner and Vilmos (*Z. anorg. Chem.*, 1899, **21**, 153) prepared the salt by a different method and found it to be anhydrous. This may account in part for the lower values obtained by Werner and Herty (*Z. physikal. Chem.*, 1901, **38**, 338) on measuring the electrical conductivity of the bromide. At 25°, for $v = 1000$ and 2000 they found $\mu = 88{\cdot}26$ and 90·94 respectively.

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LIV.—*The Cyanine Dyes. Part IV. Cyanine Dyes of the Benzothiazole Series.*

By William Hobson Mills.

The bases of the benzothiazole series were observed by Hofmann to show a marked resemblance to quinoline and quinaldine. He was consequently led to attempt, by acting with alkalis on mixtures of their alkyl iodides, to prepare from them dyes analogous to the cyanines (*Ber.*, 1887, **20**, 2262). By heating aqueous solutions of a quaternary salt of benzothiazole and the corresponding compound of 1-methylbenzothiazole with ammonia, he succeeded in obtaining substances which in fact showed, in their brilliant metallic lustre and their intense colour in solution, great similarity to the dyes of that class. He examined more particularly the compound obtained from the amyliodides, and his analysis of this substance confirmed his view that it was produced by the condensation of one molecule of benzothiazole amyliodide with one of 1-methylbenzothiazole amyliodide with the elimination of one molecule of hydrogen iodide and, probably, two atoms of hydrogen. He represented its formation by the following equation:

$$C_7H_5NS,C_5H_{11}I + C_8H_7NS,C_5H_{11}I = C_{25}H_{31}N_2IS_2 + HI + H_2$$

and regarded it as cyanine in which the quinoline nuclei were replaced by nuclei of benzothiazole.

In connexion with previous work on the cyanine dyes (T., 1920, **117**, 579, 1035, 1550) a re-examination of these compounds was undertaken. It was found that the yield of dye obtained from a mixture of benzothiazole ethiodide and 1-methylbenzothiazole ethiodide by Hofmann's method was so small as to render further work very difficult. Other methods were therefore tried and it was discovered that the condensation could be carried out much more conveniently with pyridine. A solution of the two ethiodides in pyridine, after having been heated at 100° for several hours, gives, on cooling, a crystalline deposit which consists of a purple dye mixed with a larger quantity of a bright yellow compound. The dye crystallises in prisms with a steel-blue, metallic lustre and gives intense purplish-red solutions which are decolorised by addition of excess of a mineral acid. It thus strongly resembles the *iso*cyanines, and is evidently the diethyl analogue of Hofmann's diamyl compound. It is, moreover, a powerful photographic sensitiser, conferring sensitiveness for the green, yellow, and orange regions of the spectrum. The yellow compound which is formed along with the dye is likewise a quaternary iodide and

is considerably less soluble than the dye. It is also, as Mr. F. F. Renwick informs me, according to the spectrographic investigation very kindly carried out in the laboratories of Messrs. Ilford, Limited, a powerful sensitiser, conferring sensitiveness on silver chloride emulsions for blue rays for which such emulsions are not normally sensitive.

The investigation of these two substances has led to an unexpected result. It is the yellow compound, and not the red dye as Hofmann supposed, which has proved to be the (pseudo)-cyanine (I) of the benzothiazole series. It may therefore be termed a *thiocyanine*. The purple dye has the composition required by the formula $C_{21}H_{21}N_2IS_2$. It thus contains two more carbon atoms and two more hydrogen atoms than the yellow substance, and it will be shown that there is great probability that it has the constitution II.

$$C_6H_4<{S \atop \underset{Et}{N}}>C{:}CH{\cdot}C\lessdot{S \atop \underset{Et\ I}{N}}>C_6H_4$$

(I.)

$$C_6H_4<{S \atop \underset{Et}{N}}>C{:}CH{\cdot}CH{:}CH{\cdot}C\lessdot{S \atop \underset{Et\ I}{N}}>C_6H_4$$

(II.)

If this is correct, the quinoline dyes with which it is to be compared are the carbocyanines (Pope and Mills, *Phot. J.*, 1920, **60**, 253); it is the pinacyanol of the benzothiazole series, and the name *carbothiocyanine* is proposed for the dyes of this class.

The constitution (I) of the yellow iodide (diethylthiocyanine iodide) has been established by synthesising the compound from *o*-aminophenyl mercaptan. When two molecular proportions of the latter substance are heated with one of ethyl malonate, the following condensation takes place :

$$C_6H_4<{SH \atop NH_2} + EtO_2C{\cdot}CH_2{\cdot}CO_2Et + {HS- \atop H_2N}>C_6H_4 =$$
$$C_6H_4<{S \atop N}\gtrdot C{\cdot}CH_2{\cdot}C\lessdot{S \atop N}>C_6H_4 + 2EtOH + 2H_2O.$$

The resulting "anhydro-base," dibenzothiazolylmethane, behaves as a monoacid base towards ethyl iodide, forming a monoethiodide only (III).

$$C_6H_4<{S \atop \underset{Et\ I}{N}}\gtrdot C{\cdot}CH_2{\cdot}C\lessdot{S \atop N}>C_6H_4 \quad \text{(III.)} \qquad C_6H_4<{S \atop \underset{Et}{N}}>C{:}CH{\cdot}C\lessdot{S \atop N}>C_6H_4 \quad \text{(IV.)}$$

This quaternary salt, when treated with alkalis, loses hydrogen iodide like, for example, papaverine benzyl chloride (Decker and Klauser, *Ber.*, 1904, **37**, 528) and benzyldihydro*iso*quinoline methosulphate (Hamilton and Robinson, T., 1916, **109**, 1035), and gives a yellow, crystalline base melting at 162°, which must have the constitution IV. This compound, 2-ethylbenzothiazolenylbenzothiazolylmethane, combines readily with one molecular proportion of ethyl iodide, giving a yellow, quaternary salt which proved to be identical with the yellow compound formed by the condensation of benzothiazole ethiodide with 1-methylbenzothiazole ethiodide. Although the addition of ethyl iodide to the base IV might conceivably take place in more than one way, the identity of the product with that obtained from a mixture of benzothiazole ethiodide and 1-methylbenzothiazole ethiodide shows that one ethyl group must be attached to each of the two nitrogen atoms in its molecule. The addition of ethyl iodide therefore takes place at the non-ethylated nitrogen atom of the base, and the yellow, quaternary iodide is consequently proved to have the constitution I.

The corresponding series of reactions was also carried out in the methyl series. The yellow iodide,

$$C_6H_4{<}{\overset{S\text{---}}{\underset{NMe}{}}}{>}C{:}CH{\cdot}C{\leqslant}{\overset{S\text{---}}{\underset{NMeI}{}}}{>}C_6H_4,$$

which formed the final product was found to be identical with that obtained by condensing benzothiazole methiodide with 1-methylbenzothiazole methiodide.

To gain information respecting the manner in which the purple dye is formed from the two alkyl iodides, the corresponding condensation was carried out with a mixture of benzothiazole ethiodide and 1 : 5-dimethylbenzothiazole ethiodide. The presence of the 5-methyl group in the latter substance enabled the residue of the 1:5-dimethyl compound to be identified in the condensation products, and the share taken by each ethiodide in the condensation could thus be determined. The reaction proceeded in the same manner as before, with the formation of a similar mixture of a purple dye and a yellow substance.

The composition of the yellow substance was that required by formula V.*

* The evidence at present available does not serve to distinguish between this formula for the compound and the, presumably, tautomeric formula in which the iodine is attached to the other nitrogen atom, with the corresponding shift in the double linkings.

$$C_6H_4{<}{}^{S}_{NEt}{>}C{:}CH{\cdot}C{\lessgtr}{}^{S}_{N}{>}C_6H_3{\cdot}CH_3$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Et\ \ I$$

(V.)

$$CH_3{\cdot}C_6H_3{<}{}^{S}_{NEt}{>}C{:}CH{\cdot}CH{:}CH{\cdot}C{\lessgtr}{}^{S}_{N}{>}C_6H_3{\cdot}CH_3$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Et\ \ I$$

(VI.)

$$C_6H_4{<}{}^{C_2H_2}_{NEt}{>}C{:}CH{\cdot}CH{:}CH{\cdot}C{\lessgtr}{}^{C_2H_2}_{N}{>}C_6H_4$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Et\ \ I$$

(VII.)

It was thus, as was to be expected, the monomethyl derivative of the yellow compound previously obtained, and was accordingly formed from one molecule of the ethiodide of benzothiazole and one of the ethiodide of the 1 : 5-dimethyl base.

The purple dye, however, had the composition $C_{23}H_{25}N_2IS_2$; it is thus the dimethyl derivative of the purple dye $C_{21}H_{21}N_2IS_2$ previously obtained, and therefore both the benzothiazole nuclei, which it contains, are derived from the 1:5-dimethyl compound. The two residues of this compound account for twenty-two out of the twenty-three carbon atoms in the molecule of the dye; the molecule is thus built up of these two residues and a residue consisting of one carbon atom and one or more hydrogen atoms.

Since the dye is not produced by the action of pyridine on 1-methylbenzothiazole ethiodide alone, it seems that the part which the benzothiazole ethiodide plays in its formation is to provide this monocarbon residue.

The simplest interpretation of these facts would appear to be that the latter residue is a methenyl or methylene group, through which the two residues of 1 : 5-dimethylbenzothiazole ethiodide are linked together. In consideration of the general chemical characteristics of the 1-methylbenzothiazole alkyl haloids, it is probable that such a linking would be effected through the carbon atoms of the 1-methyl groups. This view is confirmed by the relationship which can be traced between these dyes and the carbocyanines.

In the first place, there is a marked similarity in the conditions of formation of the compounds of the two series; the carbocyanines are best prepared from a mixture of a quinoline alkyl haloid and a quinaldine alkyl haloid (by the action of alkali and formaldehyde), but neither of the two quinoline nuclei present in the molecule of the dye comes from the quinoline alkyl haloid. Both are derived from the quinaldine alkyl haloid, and the dye is built up from the

residues of two molecules of the quinaldine alkyl haloid and a methenyl group. These purple benzothiazole dyes are similarly formed from a mixture of a benzothiazole alkyl haloid and a 1-methylbenzothiazole alkyl haloid, but neither of the two benzothiazole nuclei present in the molecule of the dye comes from the benzothiazole alkyl haloid. Both are derived from the 1-methylbenzothiazole alkyl haloid, and the dye is built up from the residues of two molecules of the 1-methylbenzothiazole alkyl haloid and a mono-carbon group. But whilst in the preparation of the carbocyanines as usually carried out, the methenyl group is supplied, at any rate largely, by the added formaldehyde, in these purple benzothiazole dyes the mono-carbon residue is apparently produced directly or indirectly by the decomposition of the benzothiazole alkyl haloid. There is, moreover, an exact correspondence in the composition of the dyes of the two classes; the composition of the dye from 1-methylbenzothiazole ethiodide, for example, is precisely that which would be possessed by a substance derived from pinacyanol by the replacement of the two quinoline nuclei which it contains by nuclei of benzothiazole. Secondly, there is a close agreement in the general physical and chemical characters of the two series of dyes, extending even to the fact that both are exceptionally powerful photographic sensitisers. On these grounds it is exceedingly probable that these purple dyes are analogous to the carbocyanines in structure, and accordingly that their constitution is to be represented by the formulæ of the type of II and VI corresponding with the formula of pinacyanol (VII) (Mills and Hamer, T., 1920, **117**, 1550).

It is true that there is considerable difference between the colour of the two classes of dyes; the carbocyanines are blue, whilst these benzothiazole dyes are purplish-red. Benzothiazole derivatives are, however, in general, less deeply coloured than the corresponding derivatives of quinoline. For example, the alkyl iodides of the quinoline bases are yellow; those of the benzothiazole bases are colourless, or nearly so. The *pseudo*-cyanines are red; the corresponding derivatives of benzothiazole, as is shown in this paper, are yellow. The carbocyanines of the benzothiazole series would therefore be expected to be considerably less deeply coloured than the true carbocyanines.

Photographs of the absorption spectra of these purple dyes in the visible region taken in a wedge spectrograph on a panchromatic plate show a close resemblance to those of the carbocyanines. In each case the spectrograph shows a pair of bands overlapping as the thickness of the solution increases, the less refrangible band being the deeper and the more sharply defined. The bands in

the pinacyanol spectrum are deeper, broader, and more distinctly outlined than those in the spectrum of the purple dyes from 1-methylbenzothiazole ethiodide; they are also more widely separated and lie nearer to the red end of the spectrum; but in other respects the resemblance between the spectrograms is so close as strongly to suggest a chemical relationship between the two dyes.

EXPERIMENTAL.

The benzothiazole required for this investigation was prepared by the method described by Möhlau (*Ber.*, 1888, **21**, 59) of heating dimethylaniline with sulphur. The base was found to form a sparingly soluble nitrate, and this fact was used for its purification. The crude base boiling between 200° and 260° was dissolved in concentrated hydrochloric acid (1 c.c. for 1 gram of base) and to the cold solution was added a solution of ammonium nitrate (1 gram of salt for 1·7 grams of base) in a little more than 0·5 part of water. The liquid set to a mass of crystals of benzothiazole nitrate. The salt was collected, washed with a solution of ammonium nitrate, recrystallised if necessary from water, and decomposed with sodium hydroxide.

1-Methylbenzothiazole was prepared by oxidising thioacetanilide with potassium ferricyanide (Jacobson, *Ber.*, 1886, **19**, 1072). The ethiodides of these two bases have not been previously described.

Benzothiazole ethiodide was prepared by heating a mixture of equimolecular quantities of benzothiazole and ethyl iodide for twenty-four hours at 100°. The product, which formed a pale brown, viscous mass, was crystallised from alcohol. The quaternary salt was thus obtained in almost colourless prisms melting at 138—139° (Found: I = 43·5. $C_9H_{10}NIS$ requires I = 43·6 per cent.).

1-*Methylbenzothiazole Ethiodide.*—A mixture of equimolecular quantities of 1-methylbenzothiazole and ethyl iodide was heated for forty hours at 100° and the resulting crystalline mass was recrystallised from alcohol. The ethiodide consists of stout, colourless needles melting at 190—192° (Found: I = 41·6. $C_{10}H_{12}NIS$ requires I = 41·6 per cent.).

Action of Pyridine on Mixtures of Benzothiazole Ethiodide and 1-Methylbenzothiazole Ethiodide.

Benzothiazole ethiodide (12 grams) and 1-methylbenzothiazole ethiodide (16 grams) were dissolved in pyridine (100 c.c.) and the mixture was heated in the boiling water-bath. A deep purplish-red colour rapidly developed. After heating for seven to eight hours and leaving for twelve hours, the crystalline deposit was

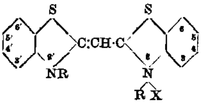
collected and digested with warm water to remove unchanged 1-methylbenzothiazole ethiodide. The mixture of thiocyanine and carbothiocyanine remaining was separated by taking advantage of the difference in density of the two compounds. On treating with carbon tetrachloride, the steel-blue prisms of the carbothiocyanine float, whilst the thiocyanine, which is coloured red by carbothiocyanine, sinks. The carbothiocyanine was thus easily obtained pure. The thiocyanine, on the other hand, contained much carbothiocyanine and was purified by extracting with successive small quantities of boiling methyl alcohol as long as these were deeply coloured and was then recrystallised from methyl alcohol, or from pyridine, until it gave a pure yellow solution.

By precipitating the original pyridine mother-liquor with dilute hydrochloric acid, in which a little potassium iodide had been dissolved, a material consisting of carbothiocyanine contaminated with tarry matter was obtained. By washing this with ether, crystallising from methyl alcohol, and floating ou carbon tetrachloride, an additional quantity of the pure dye can be isolated. The total yield of pure carbothiocyanine is usually 2—2·5 grams and that of crude thiocyanine 4—5 grams.

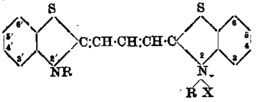
2 : 2′-*Diethylthiocyanine Iodide.**—This compound crystallises from methyl alcohol in bright yellow, prismatic needles, which melt and decompose at 311° (Found: C = 49·20; H = 4·09; I = 27·05. $C_{19}H_{19}N_2IS_2$ requires C = 48·9; H = 4·10; I = 27·22 per cent.). The yellow, alcoholic solution gives an absorption spectrum consisting, in the visible region, of a pair of absorption bands, the heads of which lie at λ 4230 and λ 4000 approximately, the former being considerably the stronger.

An investigation of the sensitising action of this compound was kindly carried out in the laboratories of Messrs. Ilford, Limited. Mr. F. F. Renwick reports that " it was found to be a very powerful

* The numbering is in accordance with the following scheme :—
Thiocyanines :—



Carbothiocyanines :—



sensitiser for silver chloride emulsions, on which it confers pronounced sensitiveness in the blue region of the spectrum, rising to a maximum lying between λ 0·45—0·46μ and falling again to zero at λ 0·49μ. The normal sensitiveness of a silver chloride emulsion lies between λ 0·36 and 0·42μ."

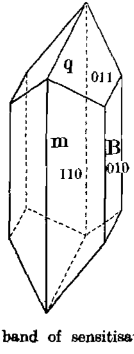
2 : 2′-*Diethylcarbothiocyanine Iodide*.—This compound crystallises in long prisms with a beautiful steel-blue lustre. It melts and decomposes at 269° (Found: C = 51·22, 51·28; H = 4·24, 4·27; I = 25·8.† $C_{21}H_{21}N_2IS_2$ requires C = 51·19; H = 4·30; I = 25·8 per cent.).

Miss I. E. Knaggs, working under the direction of Mr. A. Hutchinson, kindly determined its crystallographic constants:

Crystal System—Monoclinic: *Class*—Holohedral.
Ratio of axes $a : b : c$ 0·8299 : 1 : 0·9867
Axial angle 63° 1′
Forms observed $B = \{010\}$, $m = \{110\}$, $q = \{011\}$

Table of angles:

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
{ $B : m = (010) : (110)$	16	53° 15½′— 53° 44′	53° 31′	*	
{ $m : m = (110) : (1\bar{1}0)$	8	72 36½ — 73 12½	72 58	72° 58′	0′
{ $B : q = (010) : (011)$	20	48 20 — 48 55	48 42	*	
{ $q : q = (011) : (0\bar{1}1)$	8	82 21½ — 82 46	82 42	82 36	6′
{ $m : q = (110) : (011)$	10	48 2½ — 48 21½	48 12	*	
{ $q : m = (011) : (\bar{1}\bar{1}0)$	10	131 41 —132 6	131 49	131 48	1′
{ $q : m = (011) : (\bar{1}10)$	6	83 8 — 83 22	83 16	83 12	4′
{ $m : q = (110) : (0\bar{1}\bar{1})$	7	96 32 — 96 53	96 47	96 46	1′



The compound is moderately soluble in boiling ethyl or methyl alcohol, giving intense reddish-purple solutions. It dissolves fairly readily in chloroform and rather sparingly in acetone. In water, it is very sparingly soluble, but still sufficiently so to give a very distinctly coloured solution, which is decolorised by the addition of mineral acids, but not nearly so readily as are solutions of the *iso*cyanines or carbocyanines. The alcoholic solutions give an absorption spectrum showing a pair of bands, the heads of which lie at about λ 5590 and λ 5250, that at λ 5590 being the stronger.

The substance is a powerful photographic sensitiser; spectrographs taken on gelatino-bromide plates bathed with a dilute solution of the dye in aqueous alcohol show a fairly uniform band of sensitisation, with maxima at about λ 5900 and λ 5330,

† Mean of seven estimations.

extending from the region of the natural sensitiveness of the plate to about λ 6300, and thence diminishing gradually, to end for moderate exposures at about λ 6600.

Action of Pyridine on Mixtures of Benzothiazole Ethiodide and 1 : 5-*Dimethylbenzothiazole Ethiodide.*

1 : 5-*Dimethylbenzothiazole Ethiodide.*—Equimolecular quantities of ethyl iodide and 1 : 5-dimethylbenzothiazole, prepared by oxidising thioaceto-*p*-toluidide with potassium ferricyanide (Jacobson and Ney, *Ber.*, 1889, **22**, 907), were heated together at 100° for forty-eight hours. The resulting crystalline mass, recrystallised from alcohol, gave the pure ethiodide in colourless needles melting at 138° (Found : I = 39·7. $C_{11}H_{14}NIS$ requires I = 39·8 per cent.).

Condensation with Benzothiazole Ethiodide.—A mixture of benzothiazole ethiodide (12 grams) and 1 : 5-dimethylbenzothiazole ethiodide (16 grams) was dissolved in pyridine (100 c.c.) and heated at 100° for nine hours. After remaining for twelve hours in the cold, a little thiocyanine had crystallised. After collecting this, the filtrate was poured into water (600 c.c.) and the mixture shaken with ether. The precipitate was collected, washed with ether, digested with warm water, and then crystallised from methyl alcohol. The *mixture of thiocyanine and carbothiocyanine thus* obtained was separated by extracting the more soluble carbothiocyanine with successive small quantities of boiling chloroform until a pure yellow residue of thiocyanine was obtained. From the deep purple chloroform extracts, after the addition of rather less than an equal volume of carbon tetrachloride, the carbothiocyanine crystallised in long prisms, which were accompanied by a few crystals of the thiocyanine. The pure carbothiocyanine could then be obtained from this mixture with the aid of carbon tetrachloride. After agitation with this substance, the large prisms of the carbothiocyanine rapidly rose to the surface, whilst the smaller crystals of the thiocyanine remained suspended and could be run off with the liquid.

5(or 5′)-*Methyl*-2 : 2′-*diethylthiocyanine Iodide.*—For the examination and analysis of this compound I am indebted to Mr. W. T. K. Braunholtz.

It was obtained as yellow needles melting and decomposing at 286° (Found : C = 50·5; H = 4·34; I = 26·30. $C_{20}H_{21}N_2IS_2$ requires C = 50·0; H = 4·37; I = 26·46 per cent.).

The absorption spectrum of the alcoholic solution of this compound is very similar to that of 2 : 2′-diethylthiocyanine iodide; the heads of the two bands lie at about λ 4270 and λ 4000.

5 : 5′-Dimethyl-2 : 2′-diethylcarbothiocyanine Iodide.—This compound crystallises from methyl alcohol, ethyl alcohol, pyridine, or chloroform in long prisms with a steel-blue lustre, melting and decomposing at 285° (Found: C = 52·95; H = 4·94; I = 24·25. $C_{23}H_{25}N_2IS_2$ requires C = 53·06; H = 4·83; I = 24·4 per cent.).

The absorption spectrum of the alcoholic solution shows a strong band with a head at about λ 5630 and a weaker band with a head at about λ 5290. The sensitising effect on gelatino-bromide plates is similar to that of 2 : 2′-diethylcarbothiocyanine iodide. The band of sensitisation shows maxima at about λ 5830 and λ 5330.

Synthesis of 2 : 2′-Diethylthiocyanine Iodide.

Dibenzothiazolylmethane.—A mixture of *o*-aminophenyl mercaptan (30 grams) and ethyl malonate (19·2 grams) was heated in an atmosphere of carbon dioxide, under a reflux condenser, for four hours at 200°. Alcohol vapour was evolved and the residue crystallised on cooling. By recrystallisation from alcohol the compound was obtained in colourless needles melting at 95—96° (Found: C = 63·97; H = 3·70. $C_{15}H_{10}N_2S_2$ requires C = 63·78; H = 3·57 per cent.).

Dibenzothiazolylmethane Ethiodide.—Equimolecular proportions of dibenzothiazolylmethane and ethyl iodide were heated together for forty-eight hours at 100°. The yellow, crystalline mass of ethiodide thus obtained, recrystallised from methyl alcohol, gave long, bright yellow needles melting at 245° (Found: I = 29·05. $C_{17}H_{15}N_2IS_2$ requires I = 29·0 per cent.).

2-Ethylbenzothiazolenylbenzothiazolylmethane. — Dibenzothiazolylmethane ethiodide (0·8 gram) was shaken for four hours with a 16 per cent. solution of sodium hydroxide (30 c.c.) and ether (250 c.c.). The ether was removed and the shaking continued for two hours with a fresh quantity (100 c.c.) of ether. On evaporation, the yellow, ethereal solution thus obtained gave a residue (0·52 gram) which soon crystallised. By recrystallisation from alcohol, this gave the pure base as compact, pale yellow crystals melting at 163° (Found: C = 66·14; H = 4·62; N = 9·17. $C_{17}H_{14}N_2S_2$ requires C = 65·82; H = 4·55; N = 9·03 per cent.).

2 : 2′-Diethylthiocyanine Iodide.—The above base was heated with excess of ethyl iodide for eighteen hours at 100°. The yellow, crystalline ethiodide thus formed, after recrystallisation from alcohol, was found to be identical with the thiocyanine formed by condensing benzothiazole ethiodide with 1-methylbenzothiazole ethiodide (Found: I = 27·1. Calc., I = 27·3 per cent.). Melting point, 310—311°. Melting point of the mixture with the condensation product, 310—311°.

Synthesis of 2 : 2′-Dimethylthiocyanine Iodide.

For the greater part of the experimental work involved in this synthesis I am indebted to Mr. S. R. H. Edge.

Dibenzothiazolylmethane Methiodide.—There was some difficulty in obtaining this methiodide in the pure state, the earlier preparations containing excess of the base. The base (3 grams) was therefore heated for forty-eight hours at 50° with enough methyl iodide to dissolve it completely, and the yellow methiodide which crystallised from the solution was digested with acetone to remove the unconverted base. The methiodide was then heated for twenty hours at 50° with more methyl iodide and extracted with acetone. It crystallised from aqueous methyl alcohol in deep yellow needles which melted at 238° (Found: I = 30·7. $C_{16}H_{13}N_2IS_2$ requires I = 30·0 per cent.).

2-*Methylbenzothiazolenylbenzothiazolylmethane*.—Dibenzothiazolylmethane methiodide was shaken with excess of a concentrated solution of sodium hydroxide and ether (150 c.c. for each gram of methiodide). After the decomposition of the methiodide was complete the yellow, ethereal solution was separated and dried with sodium carbonate. The residue left after evaporation of the ether crystallised, and was recrystallised from alcohol. The base was thus obtained in small, pale yellow prisms melting at 172° (Found: C = 64·77; H = 4·38. $C_{16}H_{12}N_2S_2$ requires C = 64·81; H = 4·08 per cent.).

2 : 2′-*Dimethylthiocyanine Iodide.*—The above-described base was heated for twelve hours at 100° with excess of methyl iodide. The crystalline product was washed with alcohol and recrystallised from the same solvent and then from water (Found: I = 28·92. $C_{17}H_{15}N_2IS_2$ requires I = 28·96 per cent.). The substance was thus obtained in fine yellow needles which melted and decomposed at 279—280°.

The Condensation of Benzothiazole Methiodide and 1-Methylbenzothiazole Methiodide by Pyridine.

Benzothiazole methiodide (20 grams) and 1-methylbenzothiazole methiodide (20 grams) were dissolved in pyridine (125 c.c.) and the solution was boiled gently for six hours. The liquid gradually developed a deep magenta colour and yellow crystals separated. After remaining sixteen hours at the ordinary temperature, the dark red, crystalline deposit was collected and washed with ether and then with a little hot water. To obtain the dimethylthiocyanine iodide free from the admixed carbothiocyanine, the product was extracted with successive small quantities of boiling alcohol until

most of the carbothiocyanine was removed. It was then extracted with a small quantity of boiling pyridine and finally recrystallised from water, when it was obtained as fine yellow needles melting and decomposing at 279—280° (Found: I = 28·82, 29·00. Calc., I = 28·96 per cent.). A comparison of the compound obtained in this manner with that prepared synthetically from *o*-aminophenyl mercaptan left no doubt as to the identity of the two substances. Both products, as well as the mixture of the two, behaved exactly alike when gradually heated to their melting point, beginning to darken at about 160°, beginning to sinter at 275°, and melting and decomposing at 279—280°. Dimethylthiocyanine chloride could be readily obtained from the mixed thiocyanine and carbothiocyanine iodides by dissolving in a mixture of alcohol and concentrated hydrochloric acid. Beautiful rosettes of yellow needles separated from the warm liquid. These were collected before the liquid was quite cold, and on recrystallisation from water gave pure 2 : 2′-dimethylthiocyanine chloride in bright yellow needles melting and decomposing at 269° (Found: Cl = 10·28. $C_{17}H_{15}N_2ClS_2$ requires Cl = 10·23 per cent.).

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CAMBRIDGE [*Received, February 2nd*, 1922.]

LV.—*The Influence of Protective Colloids on the Corrosion of Metals and on the Velocity of Chemical and Physical Change.*

By JOHN ALBERT NEWTON FRIEND and REECE HENRY VALLANCE.

IN a recent communication (T., 1921, **119**, 932) attention was directed to the retarding influence exerted by protective colloids on the corrosion of iron. The interesting observation was also made that when the various colloids are graded according to their powers of inhibiting corrosion, the order is almost identical with that found by Iredale (T., 1921, **119**, 109) for their retarding influence on the decomposition of hydrogen peroxide with colloidal platinum; and a relationship between this and Zsigmondy's gold numbers for the colloids can readily be traced.

Although a considerable amount of research has been carried out on the inhibiting action of protective colloids on the rate of certain chemical changes taking place in the presence of suspensoid catalysts, notably colloidal platinum, but little attention has been

directed to their influence on the velocity of non-catalysed reactions. The authors have therefore studied a considerable number of both chemical and physical changes from this point of view, and a few of their results, which may be regarded as typical, are described in the sequel.

Corrosion of Ferrous and Non-ferrous Metals.

In their fourth report on the corrosion of non-ferrous metals, presented in 1919 to the Institute of Metals (*J. Inst. Metals*, 1919, **21**, 57), Bengough and Hudson express the opinion that quantitative determinations of corrosion by loss in weight are unsatisfactory, and refer to their table of results (*loc. cit.*, p. 63; and Friend's criticism, p. 226). The present authors find that very useful information can be obtained in this manner provided that the metals are exposed for a sufficient time to yield a much higher percentage loss than that recorded in the experiments referred to. This method, therefore, has been adopted in the sequel.

The metals chosen were in the form of chemically pure foil, cut into plates approximately 4 × 5·5 sq. cm. in area. They were usually suspended from glass hooks in gas jars containing 150 c.c. of the corroding medium and allowed to remain in a thermostat for about three weeks at approximately 18°. At the close of this period the plates were removed, rubbed free from oxide, and weighed. The results obtained were as follow:

TABLE I.

Corrosion in pure aqueous emulsoid sols.

Colloid. 0·2 Per cent. in distilled water.	Iron. Loss in weight. Gram.	Iron. Mean relative corrosion.	Zinc. Loss in weight. Gram.	Zinc. Mean relative corrosion.	Lead. Loss in weight. Gram.	Lead. Mean relative corrosion.
Water	0·0582 0·0596	100	0·0297 0·0294	100	0·1628 0·1732	100
Sucrose	0·0660 0·0665	112·4	0·0330 0·0430	128·8	0·0088 0·0083	5·1
Gum acacia	0·0323 0·0347	56·9	0·0545 0·0633	199·6	0·0268 0·0379	19·2
Dextrin	0·0355 0·0290	54·7	0·0271 0·0284	93·9	0·0007 0·0024	0·9
Starch (Potato)	0·0303 0·0339	54·5	0·0210 0·0214	71·9	0·0169 0·0149	9·5
Gelatin	0·0260 0·0222	40·9	0·0226 0·0331	94·2	0·0050 0·0039	2·6
Tragacanth	0·0132 0·0134	22·6	0·0090 0·0066	26·4	0·0038 0·0027	1·9
Egg-albumin	0·0055 0·0025	6·8	0·0102 0·0090	32·5	0·0010 0·0009	0·6
Agar	0·0005 0·0027	2·7	0·0000 0·0000	0·0	0·0028 0·0018	1·4

TABLE II.

Continuous phase—3 *per cent.* NaCl.

Colloid.	Iron. Loss in weight. Gram.	Iron. Mean relative corrosion.	Zinc. Loss in weight. Gram.	Zinc. Mean relative corrosion.	Lead. Loss in weight. Gram.	Lead. Mean relative corrosion.
None	0·0652 0·0660	100	0·0462 0·0536	100	0·0648 0·0605	100
Agar (0·1%)	0·0084 —	13	0·0060 0·0110	17	0·0055 0·0051	8·5
Agar (0·01%)	0·0430 0·0424	65	0·0347 0·0402	75	— 0·0070	11·2
Gelatin (0·1%)......	0·0426 0·0477	69	0·0337 0·0368	71	0·0075 0·0064	11·0
Gelatin (0·01%) ...	0·0571 0·0548	85	0·0458 0·0459	92	0·0154 0·0155	24·6

Experiments were also made with aluminium, but the results were irregular owing to fungoid growth in some of the solutions. Where, however, the colloid remained unchanged, there was a marked retardation apparent, as the following example shows:

Colloid in 3 per cent. NaCl solution.	Aluminium. Loss in weight. Gram.	Aluminium. Mean relative corrosion.
None	0·0028 0·0028	100
Gelatin (0·1%)	0·0012 0·0013	44·6

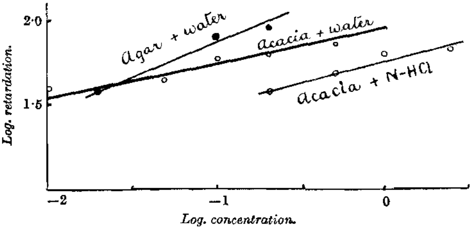
From a consideration of the foregoing results it is evident that the corrosion of non-ferrous metals, as well as of iron, is retarded by the presence of protective colloids. This is a point of considerable domestic importance, since in culinary operations colloids are invariably produced. This is probably the explanation of the very marked resistance to corrosion offered by aluminium pans. The behaviour of sucrose is interesting, for in dilute solution it is not colloidal, although not widely removed from colloid dimensions. It shows a pronounced accelerating action on the corrosion of iron (contrast T., 1921, **119**, 932) and zinc, but a powerful retarding action on that of lead. The last metal is seen to be particularly susceptible to colloid retardation.

It seemed probable that this was due to adsorption. It is not easy to estimate quantitatively the minute amount of colloid that would be adsorbed by the solid surfaces in the foregoing reactions, but it is reasonable to suppose that it would be an amount directly proportional to the retardation. Hence, writing the adsorption law as

$$\frac{x}{m} = K\sqrt[n]{C},$$

where K and n are constants, and C is the percentage concentration of the colloid, the quotient $\frac{x}{m}$ may be rendered in terms of percentage retardation. If the data are plotted as shown in Fig. 1, straight lines are obtained when the adsorption law is followed. When the results given by Friend (*loc. cit.*, p. 941) for the retarding action of various concentrations of agar and acacia on the corrosion of iron in water are plotted in this manner (Fig. 1), the curves are seen to approximate to straight lines, provided that the colloids are not excessively dilute. At great dilution the law is not followed either in corrosion experiments or in others described below.

FIG. 1.



Dissolution of Metals in Acids.

The effect of various concentrations of different colloids on the rate of dissolution of iron and zinc in dilute sulphuric acid has been examined, the mode of procedure being similar to that described above. In the case of zinc, the results obtained were extremely divergent owing to unequal "pitting" of the metal, but with iron no difficulty was experienced. Sheets of the metals were immersed in $N/2$-sulphuric acid for ten hours at about 18°. The results for iron are given in Table III, and show that the rate of dissolution is retarded by the colloids, whilst a molecularly disperse substance like sucrose has no decisive effect. When arranged according to retarding influence, the order of the colloids is again similar to that already mentioned.

It had already been noted by Friend and Dennett (this vol., p. 41) that protective colloids retarded the rate of solution of iron in acid, but no systematic study of the reaction had been made. A few experiments carried out by Mr. Trobridge with iron

TABLE III.

Continuous phase—$N/2\text{-}H_2SO_4$.

Colloid.	Colloid per cent.	Relative corrosion.	Colloid per cent.	Relative corrosion.	Colloid per cent.	Relative corrosion.
None	—	100	—	100	—	100
Sucrose	0·01	94·1	—	—	0·2	103·4
Gum acacia ...	,,	85·3	0·1	52·4	,,	77·1
Dextrin	,,	71·4	,,	79·7	,,	72·7
Starch (Potato)	,,	71·3	,,	72·2	,,	78·4
Agar	,,	68·3	,,	59·9	,,	59·5
Egg-albumin ...	,,	48·9	,,	59·3	,,	34·2
Gelatin	,,	42·0	,,	26·1	,,	15·9

immersed in N-hydrochloric acid and various concentrations of gum acacia have yielded the following results.

Acacia per cent.	0	0·001	0·01	0·05	0·10	0·20	0·50
Loss in weight of iron ...	0·0384	0·0385	0·0227	0·0211	0·0152	0·0144	0·0112
Retardation per cent.	—	—	40·9	45·1	60·4	62·5	70·8

Except in the case of the most dilute solution (0·001 per cent.) these results obey the adsorption law within the error of experiment, as shown in Fig. 1.

Rate of Dissolution of Salts in Water.

The rate of solution of salts in water has not in general been closely investigated, although it is well known that temperature, hydration, and the magnitude of the solubility coefficient are important factors. In order to determine what effect, if any, protective colloids exert on the rate of solution, potassium sulphate and chlorate were chosen for several reasons. Not only can they readily be obtained in crystals of uniform size, but they are anhydrous, and dissolve with relative slowness in water at room temperature. Crystals, measuring approximately 0·6 cm. across, were selected from samples of the commercially pure salts, and suitable weights (namely, K_2SO_4 8 grams; $KClO_3$ 5 grams) were placed in each of six small bottles of about 70 c.c. capacity, together with 50 c.c. of the solvent. The bottles were attached to a horizontal bar, which was rotated at about 50 revolutions per minute round its long axis by means of an electric motor, in a large thermostat filled with water. At stated intervals different bottles were detached, in every case one bottle with water only as solvent being chosen to serve for comparison. The liquid contents were filtered through glass wool, collected in dishes, and evaporated to

dryness, the residue being dried at 130° in an electric oven. The weights of salt per 100 grams of water, as determined in this manner, are given in the following table.

TABLE IV.

Salt.	Time in *minutes.*	*Temp.*	Percentage conc. of *salt dis-* solved in *water only.*	*Colloid.*	*Colloid* per *cent.*	Percentage *conc. of* salt dis- *solved in* colloid *solution.*	Retar- *dation* per *cent.*
K_2SO_4	10	18·7°	7·462	Agar	0·02	7·096	4·9
	60		10·279			10·095	1·8
	240		10·857 (Saturated)			10·785	0·6
K_2SO_4	20	10·5	7·620	Egg-albumin	0·10	7·466	2·02
	,,			Gelatin	,,	7·505	1·51
	,,			Gum acacia	,,	7·533	1·14
	,,			Sucrose	,,	7·786	—
$KClO_3$	10	12·2	3·851	Agar	0·02	3·636	5·58
	30	12·2	5·318		,,	5·118	3·76
	1440	8·2	4·570 (Saturated)		,,	4·591	—
$KClO_3$	15	9·1	4·002	Agar	0·03	3·935	1·63
			3·997		0·05	3·943	1·43
					0·10	3·377	15·6
					0·20	3·332	16·7

The retardation in the rate of solution is very marked, and the order for the different colloids is substantially the same as in the previous experiments. The retardation increases progressively with the colloid concentration, but if sufficient time be allowed, the same amount of salt will be dissolved eventually as if no colloid were present. The results do not appear to obey the adsorption law, but this may be due to "salting out" of the protective colloid.

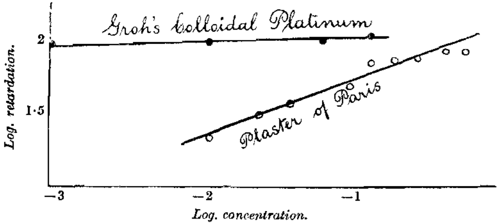
Noyes and Whitney (*Z. physikal. Chem.*, 1897, **23**, 689) showed that the rate of solution of a solid in a solvent is a function of the rate of diffusion, the film of liquid immediately in contact with the solid being a saturated solution which diffuses into the more dilute layers. The concentrations of the protective colloids in the present experiments, however, are too dilute to affect appreciably the rate of diffusion, and the cause of the reduced rate of solution thus appears to lie in some surface phenomenon. The influence of sugar is interesting, in that it accelerates the rate of solution just as it tends to accelerate the rate of corrosion of iron and zinc. The reason for this is not apparent.

No experiments have been carried out by the authors on the reverse change, namely, the rate of crystallisation of substances

from solution. A few tests have been made on the rate of setting of plaster of Paris in the presence of varying concentrations of agar. The results are shown in Fig. 2 and conform very closely to the requirements of the adsorption law.

The Liesegang ring formation is apparently another illustration of the same phenomenon. When the silver nitrate solution is added to a slab of gelatin impregnated with dichromate, colloidal silver chromate can be seen ahead of the rapidly forming rings, the space between the successive rings being determined by the difference between the rates of diffusion and of precipitation in the gel. This explanation is much less involved than that of McGuigan (*Science*, 1921, **54**, 78), and is not open to the same objections as Ostwald's theory. It receives further support from the observation of Svedberg (*Kolloid Z.*, 1909, **5**, 318) that the

Fig. 2.



reduction of chloroauric acid in alkaline solution by hydrazine hydrochloride is retarded by gelatin.

In conjunction with Messrs. D. W. Hammond, B.Sc., and J. S. Tidmus, B.Sc., it has been found that protective colloids retard the precipitation of lead and copper by metallic iron from lead acetate and copper sulphate solutions; the same is true for metallic zinc in solutions of lead and nickel salts, and in each case that has so far been investigated the results follow the adsorption law. It seems fairly clear, therefore, that protective colloids tend to retard the rate of coalescence of molecules, as well as the rate of dispersion of molecular aggregates.

Chemical Reactions not accompanied by Change of State.

In 1891, Reformatsky (*Z. physikal. Chem.*, 1891, **7**, 34) found that 1·25 per cent. agar solution had no influence on the velocity

of the acid catalysis of methyl acetate. This, in view of the foregoing results, is to be expected, for if the phenomenon is purely one of adsorption, it follows that any retarding action exerted by protective colloids would be reduced to a minimum in such systems as involve no change of state. The reaction between ammonium persulphate and potassium iodide was therefore studied in dilute solution, in the presence of sodium thiosulphate to keep in solution the iodine normally liberated by the interaction of the first two salts. A trace of starch was added to indicate when the thiosulphate bad been used up. The solutions were made up as follow: 10 c.c. of $N/2$-$(NH_4)_2S_2O_8$; 60 c.c. of H_2O or 0·1 per cent. colloid; 20 c.c. of $N/20$-$Na_2S_2O_3$ + a trace of starch. To the above mixtures 10 c.c of $N/2$-potassium iodide solution were added and the times noted at which the blue colour appeared. The results were as follow:

Colloid....	None.	Agar.	Acacia.	Albumin.	Gelatin.	Sucrose.
Time.........	33′ 20″	35′ 15″	32′ 35″	33′ 0″	32′ 50″	31′ 55″

The experiments were tried in a variety of ways, but always with the same type of result. Whilst a slight retardation was apparent in the case of agar, it was very much smaller than that observed where change of state of one or more of the components was involved. The other colloids exerted an almost negligible effect, whilst the sucrose, as in certain of the corrosion and solubility experiments, stimulated the action to a slight extent.

Suspensoid Catalysts.

Mention has already been made of the reduced catalytic activity of inorganic hydrosols in the presence of protective colloids. In the light of the preceding experiments it would appear that this is simply another manifestation of the same phenomenon. This is confirmed by the fact that if Groh's results (*Z. physikal. Chem.*, 1914, **88**, 414), on the relative times required to decompose 50 per cent. of a hydrogen peroxide solution in the presence of varying quantities of gelatin are calculated in terms of adsorption, the data are seen (Fig. 2) to conform to the adsorption law.

Conclusion.

1. It appears to be a general law that ***protective colloids tend to retard the velocity of such reactions, whether chemical or physical, as involve a change of state from solid to liquid, or vice versa, in one or more of the components.***

2. This is due to adsorption, and in many cases the adsorption law is obeyed.

3. The reduced catalytic activity of inorganic hydrosols in the presence of protective colloids is due to the same phenomenon.

4. The Liesegang phenomenon is attributable to the same cause.

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BIRMINGHAM. [*Received, January* 16*th*, 1922.]

LVI.—*Some Reactions of Benzanthrone.*

By ARTHUR GEORGE PERKIN and GEORGE DOUGLAS SPENCER.

As is well known, when fused with alkali at a temperature up to 230°, benzanthrone gives a colouring matter known as violanthrone (III).

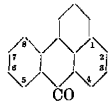
Experiments carried out at a lower temperature (180—190°) and with a less concentrated alkali indicated that in these circumstances benzanthrone is little attacked, whereas in the presence of an oxidising agent, a substance soluble in alkaline solution with a green fluorescence is produced in trifling amount. The present work originated with this observation and the desire to ascertain the nature of this substance. After numerous experiments the following method for its preparation was adopted.

Benzanthrone (2 grams), prepared in the paste form by solution in sulphuric acid and reprecipitation with water, was admixed with potassium hydroxide (12 grams), water (3 c.c.), and potassium chlorate (0·7 gram), and the mixture heated in a closed metal tube at 230—240° for three to four hours. When cold, the melt was mixed with water, and the product, which consisted of colouring matter suspended in a highly fluorescent liquid, was nearly neutralised with acid, well boiled, filtered, and extracted with very dilute potassium hydroxide solution. The insoluble residue consisted mainly of violanthrone contaminated with a small amount of a compound sparingly soluble in benzene with a reddish-violet coloration. The combined alkaline filtrates, on acidification, deposited a dull yellow, colloidal precipitate which, when collected and dried, amounted to 0·5 gram.

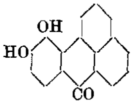
This substance (Found: C = 82·52; H = 3·83 per cent.) had all the properties of the hydroxybenzanthrone obtained by the action of sulphuric acid and glycerol on 2-hydroxyanthranol (D.R.-P.

187495; Perkin, T., 1920, **117**, 698). Its identity with this compound was confirmed by the preparation of the acetyl derivative, m.p. 200—201° (*Found*: C = 79·64; H = 4·0 per cent.), the oxonium sulphate (Found: C = 59·04; H = 3·37 per cent.), and a mixed melting-point determination of the acetyl derivative from both products. In this communication, it is referred to as β-hydroxybenzanthrone. Benzanthrone, as was perhaps to be expected, evidently behaves towards alkali like anthraquinone itself, which, as is well known (D.R.-P. 186526), yields alizarin on fusion with sodium hydroxide in the presence of sodium chlorate; this change is explained by Bucherer as due to quinonoid addition (" Lehrbuch der Farbenchemie," 1914, p. 328).

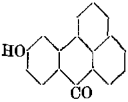
In the case of benzanthrone, the reaction does not proceed further than the formation of one hydroxyl group, a fact difficult to understand if this group is in the 7-position (II), as was previously suggested by analogy with benzalizarin (I).



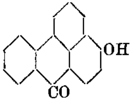
Benzanthrone.



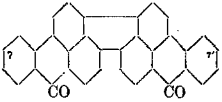
(I.)



(II.)



(III.)



(IV.)

Such a difference in behaviour would be more readily accounted for if the hydroxyl group were situated in the position 2 (III). In support of this suggestion is the extreme stability of this hydroxybenzanthrone towards fused alkali, even at as high a temperature as 240—250°, for experiment showed that after treatment in this manner the great bulk may he recovered unchanged. As henzanthrone in these circumstances yields violanthrone (IV), it would seem likely that 7-hydroxybenzanthrone under the same conditions would be converted into 7 : 7′-dihydroxyviolanthrone. That this is not the case is again readily understood if the hydroxyl group in this hydroxybenzanthrone is in position 2. With the object of determining the position of the hydroxyl group in benzalizarin, the process of methylation was adopted (*loc. cit.*), and it was evident from the ready production of the dimethyl ether that a hydroxyl group

in the ortho-position to the carbonyl group could not be present, and benzalizarin must therefore be the 7 : 8-dihydroxy-derivative. As suggested above, it now appeared to be doubtful if the position of the hydroxyl group in hydroxybenzanthrones prepared from hydroxyanthraquinones by means of sulphuric acid and glycerol can be deduced by analogy from those present in benzalizarin (*loc. cit.*), and in order, if possible, to decide this point, a study of the hydroxybenzanthrone derived from 1-hydroxyanthraquinone has now been carried out.

In order to obtain this substance, 1-hydroxyanthraquinone, prepared from sodium anthraquinone-1-sulphonate, was heated with glycerol and sulphuric acid in the presence of aniline sulphate (D.R.-P. 187495). A concentrated alcoholic extract of the dark green, amorphous product was poured into much ether, the tarry deposit removed, the solution well washed with water and evaporated. The granular residue was crystallised twice from pyridine, which removed a red impurity, and finally from acetic acid. The yield of the pure compound was approximately 25 per cent. (Found: C = 82·95; H = 4·10. $C_{17}H_{10}O_2$ requires C = 82·93; H = 4·02 per cent.). This substance, here referred to as α-hydroxybenzanthrone, consists of long, silky, yellow needles, m. p. 178—179°, soluble in sulphuric acid with an intense green fluorescence. It is insoluble in solutions of the alkali hydroxides and ammonia in the cold, but slightly soluble on boiling; with alcoholic potassium hydroxide, it gives a yellow potassium salt, and addition of sulphuric acid to its solutiou in boiling acetic acid causes the deposition, on cooling, of an oxonium sulphate in red needles. This, owing to its unstable character, was not analysed. In order to methylate α-hydroxybenzanthrone, to this substance (3 grams), in boiling methyl alcohol (90 c.c.) containing a large quantity of methyl iodide (37 c.c.), potassium hydroxide (15 grams) dissolved in methyl alcohol (75 c.c.) was added drop by drop during two days. The product, after removal of methyl iodide and concentration, was poured into ether, the ethereal solution washed with water, and then treated with a little alcoholic potassium hydroxide. The precipitate, which was formed in considerable amount, proved to consist of potassium α-hydroxybenzanthrone. The filtrate was washed with water and evaporated to dryness, and the viscid residue dissolved in a little alcohol. On cooling, yellow needles separated, which melted at 177—179° and again consisted of unattacked α-hydroxybenzanthrone. From the mother-liquor no crystalline product could be isolated.

The result of this experiment, in which such large amounts of both potassium hydroxide and methyl iodide were employed, makes

it evident that the hydroxyl group in α-hydroxybenzanthrone is resistant to methylation, and cannot therefore be in the position 8.

Ethylation by the same method was now studied, employing 2 grams of α-hydroxybenzanthrone, 60 c.c. of alcohol, 25 c.c. of ethyl iodide, and 5 grams of potassium hydroxide in 25 c.c. of alcohol. The product, after concentration, was poured into ether, the ethereal solution washed, and then treated with a little alcoholic potassium hydroxide, which caused the production of a voluminous yellow precipitate of potassium α-hydroxybenzanthrone. The ethereal filtrate, after washing with water, gave a viscid residue, from which yellow needles in small amount separated on keeping. These were purified by recrystallisation from alcohol and weighed 0·4 gram (Found: C = 83·47; H = 5·49; EtO = 16·31. $C_{17}H_9O{\cdot}OEt$ requires C = 83·21; H = 5·11; EtO = 16·42 per cent.). The residue from the Zeisel determination was found to consist of α-hydroxybenzanthrone.

The *ethoxybenzanthrone* thus obtained consisted of pale yellow needles which melted at 125—126° and dissolved in sulphuric acid to form a green, fluorescent solution. It is clear that α-hydroxybenzanthrone is ethylated only with difficulty under these conditions, but the fact that it yields an ethyl derivative more readily than a methyl derivative is in harmony with the previous experience of compounds of this character (T., 1911, **100**, 1721). α-Ethoxybenzanthrone resembles the β-methoxy-derivative previously described (*loc. cit.*, p. 298) in yielding oxonium derivatives. Thus 0·5 gram in 20 c.c. of acetic acid gave with 0·5 gram of anhydrous ferric chloride an immediate precipitate of dark red needles of the *ferrichloride.* These were washed with glacial acetic acid and dried. In the presence of water they are readily decomposed, and this method was employed for their analysis (Found: $C_{19}H_{14}O_2$ = 57·91; Fe = 11·59; Cl = 29·81. $C_{19}H_{14}O_2,HFeCl_4$ requires $C_{19}H_{14}O_2$ = 57·95; Fe = 11·80; Cl = 30·05 per cent.).

With fuming stannic chloride in the presence of acetic acid, α-ethoxybenzanthrone gives at first a dark red solution possessing a green fluorescence, and from this bright red needles of the *stannichloride* almost immediately separate [Found: $C_{19}H_{14}O_2$ = 67·59. $(C_{19}H_{14}O_2)_2,SnCl_4$ requires $C_{19}H_{14}O_2$ = 67·73 per cent.].

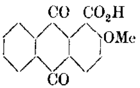
Oxidation of β-Methoxybenzanthrone.

It has been previously shown (T., 1920, **117**, 698) that β-methoxybenzanthrone, obtained by the methylation of β-hydroxybenzanthrone, when oxidised with chromic acid, yields a crystalline acid in small amount, which was suspected to consist of a methoxyanthra-

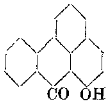
quinone-α-carboxylic acid. As it was now of some importance to be certain that this was the case, the decomposition was again studied, employing 1 gram of β-methoxybenzanthrone, 12 c.c. of acetic acid, and 1 gram of chromic acid in 2 c.c. of 50 per cent. acetic acid. When effervescence had ceased, hot water was added, and after keeping over-night the semi-crystalline precipitate was collected. This was dissolved in hot dilute ammonia, filtered, the orange liquid acidified, and the crystals which separated on cooling were again submitted to the same treatment, the ammoniacal liquid previous to acidification being, however, digested with a little animal charcoal.

The colourless needles thus obtained melted at 276—277° and weighed 0·1 gram (Found: C = 67·97; H = 3·48. $C_{16}H_{10}O_5$ requires C = 68·08; H = 3·54 per cent.).

There could be little doubt, therefore, that this compound was a β-methoxyanthraquinonecarboxylic acid, and this was confirmed by the fact that it was found to be identical with the acid (V)



(V.)



(VI.)

which has been obtained by Bradshaw and Perkin in another way. An account of this will shortly be laid before the Society.

There seems to be little doubt, therefore, as was suggested earlier in this paper, that the β-hydroxybenzanthrone which is formed either by the fusion of benzanthrone with alkali and an oxidising agent, or from 2-hydroxyanthranol, glycerol, and sulphuric acid, is the 2-hydroxy-compound (III).

Moreover, it is clear, from the behaviour of α-hydroxybenzanthrone when submitted to methylation, that this substance must contain the hydroxyl group in the position 4 or 5 adjacent to the carbonyl group, and of these, position 4 appears to be preferable (VI) on account of the fluorescence which the substance exhibits in sulphuric acid solution.

The suggestion made in the previous communication (*loc. cit.*), that the position of the hydroxyl groups in hydroxybenzanthrones prepared from hydroxyanthraquinones by means of glycerol and sulphuric acid might be inferred by reference to the constitution of benzalizarin, is accordingly untenable, and it is evident that the constitution of the hydroxybenzanthrones obtained from mono- or

di-hydroxyanthraquinones which contain free α-positions in the hydroxylated ring can only be determined by experiment.

Interesting in this connexion would be the dihydroxybenzanthrone derived from purpuroxanthin (1 : 3-dihydroxyanthraquinone), but, unfortunately, although numerous attempts to prepare this compound have been made using the ordinary conditions, only mere traces have been obtained. The main product has hitherto consisted of an ochre-yellow, amorphous compound, which certainly is not the desired dihydroxy-derivative. Further experiments with regard to this reaction are, however, still in progress.

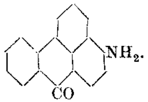
An Improved Method for the Preparation of 2-Hydroxybenzanthrone.

During some more recent experiments on the preparation of 2-hydroxybenzanthrone from benzanthrone, fused alkali, and potassium chlorate, it was observed that when the benzanthrone employed contained anthraquinone as impurity, the yield of the hydroxy-compound was substantially increased. As the result of further investigation, it has been ascertained that if a considerable amount of anthraquinone is present in the fusion mixture, an almost quantitative conversion of benzanthrone into the hydroxy-compound can be effected.

As an example of this method, a mixture of benzanthrone (50 grams), 94 per cent. anthraquinone (50 grams), alkali hydroxide (300 grams), potassium chlorate (35 grams), and water (75 c.c.) was heated at 250° * in an oil-jacketed autoclave provided with a stirrer during one and a half hours, and then at 250—265° * during three hours. The melt, when cold, was diluted with boiling water, filtered, and the insoluble residue extracted with boiling water until nothing more dissolved. The highly fluorescent filtrate, on neutralisation with acid, deposited yellow flocks of 2-hydroxybenzanthrone, which, when collected and dried, weighed, on the average, 40·5 grams, equivalent to 86 per cent. of the theoretical amount. By acetylation, the product yielded yellow needles melting at 200—201°, identical with the 2-acetoxybenzanthrone previously described (Found: C = 79·00; H = 4·15 per cent.). The residue insoluble in alkali (approximately 37 grams) † was of a grey colour and consisted of anthraquinone mixed with a little unattacked benzanthrone. It could be employed in a second operation, or the anthraquinone could be recovered by sublimation. As was to be anticipated, some destruction of the anthraquinone occurs during the fusion process, and this is shown by the presence of phthalic acid, which could be

* Temperature of the oil jacket. † This amount was variable.

extracted by means of ether from the acid filtrate from the precipitated hydroxybenzanthrone. The anthraquinone in this fusion process is evidently the main oxidising agent and may act also as a carrier of oxygen between the chlorate and the benzanthrone, although it is somewhat remarkable that good results have hitherto only been obtained by employing it in large amount. It is interesting to observe that in the absence of the chlorate, anthraquinone itself can be employed as the oxidising agent, but the yield of 2-hydroxybenzanthrone is then by no means so satisfactory as when the chlorate is also present. The hydroxybenzanthrone thus produced is much purer than that obtained from 2-hydroxyanthranol by means of glycerol and sulphuric acid, and owing to the readiness with which it can be prepared in a state of purity by this method a study of its derivatives will now be undertaken.

2-Aminobenzanthrone, 

This substance can be readily obtained by heating 2-hydroxybenzanthrone with strong ammonia under pressure.* A mixture of 2-hydroxybenzanthrone (25 parts) and ammonia (*d* 0·880; 500 parts) was heated in an oil-jacketed autoclave gradually to 220° and maintained at from 220—230° (temperature of the oil-jacket) for seven hours. When cold, the product, diluted with water, was filtered, and unchanged 2-hydroxybenzanthrone present in the filtrate as ammoniun salt was recovered by acidification. The dull red crystals of the aminobenzanthrone remaining on the filter were collected, washed with dilute alkali, and purified by crystallisation from alcohol (Found: C = 83·04; H = 4·68; N = 5·55. $C_{17}H_{11}ON$ requires C = 83·26; H = 4·50; N = 5·71 per cent.). Thus obtained, it consisted of bright red needles melting at 223—224°, which dissolve in alcohol with the formation of an intensely fluorescent solution.

By acetylation in the usual manner, an *acetyl* derivative was obtained, and this crystallised from acetic anhydride in yellow needles melting at 264—265° (Found: N = 5·08. $C_{19}H_{13}O_2N$ requires N = 4·88 per cent.).

The *benzoyl* derivative was readily produced by heating aminobenzanthrone with 5 parts of benzoic anhydride at 180° for one

* These processes for the preparation of 2-hydroxybenzanthrone and 2-aminobenzanthrone have been protected by a provisional patent.

hour. By crystallisation from alcohol, it was obtained as pale yellow needles melting at 238—239° (Found: C = 82·38; H = 4·43; N = 4·22. $C_{24}H_{15}O_2N$ requires C = 82·52; H = 4·30; N = 4·01 per cent.).

The re-conversion of the amino-derivative into the β-hydroxy-compound was carried out under the following conditions.

Crude aminobenzanthrone (2 grams) in 15 c.c. of sulphuric acid was cooled to 0°, and 1 gram of sodium nitrite added, with stirring. After one hour, the product was poured into water and the solution boiled, when dull yellow flocks separated. These were collected, extracted with dilute ammonia, the extract was acidified, and the precipitate collected and dissolved in a minimum of alcohol. The solution, when diluted with much ether, deposited an amorphous impurity, and the clear liquid, on evaporation, now yielded a bright yellow residue.

This substance, which dissolved in dilute alkali, forming a green fluorescent, yellow solution, appeared to consist of 2-hydroxybenzanthrone, and this was rendered certain by the preparation of its acetyl derivative, which was obtained as yellow needles melting at 199—200°.

Acetylaminobenzanthrone (1 gram in 15 c.c. of acetic acid) was readily oxidised by the addition of 1·5 grams of chromic acid in 50 per cent. acetic acid solution. The liquid was cooled, allowed to stand over-night, diluted with water, and the brown precipitate was collected. This, on extraction with boiling dilute ammonia, gave at first a deep blue solution, which, on treatment with animal charcoal, became pale orange. Addition of hydrochloric acid caused the deposition of crystals, which, after re-solution in ammonia and subsequent acidification, consisted of salmon-pink needles, m. p. 250—252° (Found: N = 5·46. $C_{15}H_9O_4N$ requires N = 5·24 per cent.). The yield of this compound, which may consist of 2-amino-anthraquinone-1-carboxylic acid, has hitherto been too small to permit of its satisfactory examination, but experiments are in progress with the hope of preparing it in a more economical manner.

No description of 2-aminobenzanthrone could be found in the patent literature available, but in a footnote to the paper by Bally and Scholl on benzanthrone (*Ber.*, 1911, **44**, 1658) it is stated that, according to a patent application (French Pat. 23880 of 1908), 2-aminobenzanthrone is produced by heating 2-aminoanthranol, glycerol, and sulphuric acid (82 per cent.).

As there was no means of ascertaining if the product thus obtained is identical with that produced from 2-hydroxybenzanthrone by means of ammonia otherwise than by experiment, 2 grams of 2-aminoanthranol (from 2-aminoanthraquinone, aluminium powder,

and sulphuric acid) in 50 grams of sulphuric acid (62° Bé.) were heated gradually to 120° and subsequently at 128°. The liquid, on dilution with water, deposited orange-red flocks, which were collected, dried, and extracted with alcohol. The concentrated extract was poured into ether, causing the precipitation of a resinous impurity, a further amount being deposited by washing the ethereal solution with water. On evaporation of the ethereal solution, a red powder was obtained, which crystallised from alcohol in needles melting at 223—224° and gave an acetyl derivative melting at 264—265°. As the result of mixed melting-point determinations, these substances proved to be identical with the 2-aminobenzanthrone and 2-acetylaminobenzanthrone described above.

A further study of these compounds is in progress.

We are indebted to Mrs. Metcalfe (*née* Pauline O'Neill) for help in the earlier experiments described in this paper, and to the British Dyestuffs Corporation, Ltd., for many facilities in carrying out this work.

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LVII.—*Organo-derivatives of Thallium. Part V. The Preparation of Thallium Diaryl Salts.*

By ARCHIBALD EDWIN GODDARD and DOROTHY GODDARD.

IN Part III of this work it was shown that mercury diaryls and aromatic bismuthines of the type R_3Bi could be used in the preparation of thallium diaryl haloids. It was pointed out that lead triethyl chloride, when treated with thallic chloride in dry ether, gave rise to lead diethyl chloride and thallous chloride. By substituting lead tetraethyl for lead triethyl chloride, the authors now find that the same products result and the reaction is therefore represented by the equation :

(1) $Et_4Pb + TlCl_3 = Et_2PbCl_2 + Et_2TlCl$.
(2) $Et_2TlCl = TlCl + C_4H_{10}$.

Although thallium diethyl chloride is very stable under ordinary conditions, the above equations are, according to the products obtained, the only ones which represent the reactions. Moreover,

it has been very noticeable so far that reactions carried out between lead alkyl compounds and thallic chloride always lead to the production of thallous chloride; this must be due in some way to the presence of lead. This reaction is comparable with the action of thallic chloride on tin tetraethyl, for although the presence of tin diethyl chloride, thallium diethyl chloride, and thallous chloride was shown, prolonged boiling of the mixture with water tended towards the production of more thallous chloride and the disappearance of thallium diethyl chloride. Grüttner and Krause (*Ber.*, 1916, **49**, 1125) prepared lead methyl triethyl in 90 per cent. yield by the action of magnesium methyl chloride on lead triethyl bromide.

Using magnesium methyl iodide, we now find that the yield is almost the same, and the boiling point recorded by the previous investigators (70—70·5°/16 mm.) has been confirmed. Lead methyl triethyl reacts with thallic chloride according to the equation: $Et_3PbMe + TlCl_3 = Et_3PbCl + TlCl + MeCl$. This agrees with Grüttner and Krause's observation that the lead compound, when treated with halogen, splits off the methyl group, giving lead triethyl haloid. It has already been shown that lead tetraphenyl reacts with thallic chloride, producing lead diphenyl chloride and thallium diphenyl chloride, and this reaction has now been extended to mixed lead tetra-aryls and arylalkyls. Lead diphenyl diethyl (Moller and Pfeiffer, *Ber.*, 1916, **49**, 2441) was stated partly to decompose on distillation. We have confirmed this statement, and the product now used distilled at 182°/16 mm. The above investigators pointed out that this compound, when treated with hydrogen chloride, gives rise to lead diethyl chloride, and this observation now receives support from the action of thallic chloride, which yields lead diethyl chloride and thallium diphenyl chloride. Lead diphenyl di-α-naphthyl, m. p. 197° (Krause and Schmitz, *Ber.*, 1919, **52**, [*B*], 2150), was prepared with the object of finding which groups the thallium would split off, and it was again observed to be the heavier ones, the products of reaction being lead diphenyl chloride and thallium di-α-naphthyl chloride. The general equation for these reactions appears to be $R'_2PbR_2 + TlCl_3 = R'_2PbCl_2 + R_2TlCl$, where R' is the smaller group.

Since bismuth triaryls give thallium diaryl compounds, and triphenylstibine yields triphenylstibine dichloride, the organo-derivatives of the other metals of group V of the type of R_3M have been studied in their reactions towards thallic chloride. Triphenylphosphine (Pfeiffer, *Ber.*, 1904, **37**, 4620) yields thallous chloride and unchanged phosphine, this change probably taking place in two stages:

(1) $Ph_3P + TlCl_3 = Ph_3PCl_2 + TlCl$.
(2) $Ph_3PCl_2 = Ph_3P + Cl_2$.

This view is substantiated by the fact that triphenylphosphine dichloride has never been isolated, the syrup obtained by direct chlorination of triphenylphosphine yielding chlorobenzene and diphenylphosphine chloride on distillation. With triphenylarsine in the cold, the products are thallous chloride and traces of phenylarsenious dichloride, and in the hot, thallous chloride, thallium diphenyl chloride, and triphenylarsine dichloride.

1-Acetoxymercuri-β-naphthol (Bamberger, *Ber.*, 1898, **31**, 2624) reacts with thallic chloride to yield thallous and mercurous chlorides, the naphthalene nucleus being completely disrupted.

Hitherto no salts of thallium diaryl compounds have been made, and the authors find that they are much more difficult to obtain than the corresponding aliphatic derivatives. The thallium dialkyl hydroxides are prepared by the action of moist silver oxide on the haloid compounds, but by using a large excess of alcoholic potash and thallium diphenyl chloride, *thallium diphenyl oxide,* and not the hydroxide, is formed. This behaviour is analogous to the formation of diphenylarsenious oxide from the corresponding chloride. It appears to be more soluble in organic solvents than lead diphenyl oxide, and it is decidedly basic in character, readily combining with nitrophenols, nitrocresols, nitroso-compounds, and oximes; the substances thus formed are at present under investigation. By dissolving this oxide in glacial acetic acid, *thallium diphenyl acetate* was isolated. *Thallium diphenyl nitrate* was formed by the interaction of silver nitrate and thallium diphenyl bromide in xylene, prolonged boiling being required to obtain a good yield. The *nitrite, chromate,* and *pyrophosphate* were obtained in a similar manner. The nitrite and nitrate are more insoluble than the corresponding alkyl compounds, and the chromate is not so intensely coloured, neither is it as explosive (Goddard, T., 1921, **119**, 672). The nitrate and acetate do not contain water of crystallisation, as is the case with the analogous lead diphenyl compounds (Polis, *Ber.*, 1887, **20**, 716, 3331), and thallium diphenyl acetate has a much higher melting point than the corresponding derivative of lead.

The method of estimation of the thallium in organo-derivatives is now appended and also a means of analysis of halogen in organo-derivatives of thallium, lead alkyl haloids, and mercury derivatives, which is a modification of the Carius method and more rapidly carried out.

EXPERIMENTAL.

Action of Thallic Chloride on Lead Tetraethyl.

To a solution of 1·05 grams of lead tetraethyl in dry ether, 1·5 grams of thallic chloride in the same solvent were added, when a white, amorphous precipitate immediately appeared. Having been refluxed for twenty minutes, the mixture, on filtration, yielded 0·65 gram of thallous chloride. Evaporation of the ether gave 1·0 gram of yellow needles, identified as lead diethyl chloride.

Action of Thallic Chloride on Lead Methyl Triethyl.

To a solution of 1·09 grams of thallic chloride in 2·7 c.c. of dry ether, 1·09 grams of lead methyl triethyl were added. A white precipitate appeared, and after boiling for thirty minutes the whole was allowed to stand over-night and was then filtered hot. The residue (0·84 gram) was thallous chloride, and the filtrate on evaporation gave 1·2 grams of long needles, identified as lead triethyl chloride (Found: Cl = 11·15. Calc., Cl = 11·69 per cent.).

Action of Thallic Chloride on Lead Diphenyl Diethyl.

To 2·2 grams of lead diphenyl diethyl (prepared by the action of magnesium ethyl bromide on lead diphenyl bromide) in 20 c.c. of ether, 1·6 grams of thallic chloride in 4·5 c.c. of the same solvent were added. A bulky, white solid separated immediately, and after one and a half hours the whole was filtered. The residue was heated under reflux with alcohol and filtered hot, when 1·9 grams of solid, which was found to be thallium diphenyl chloride, were obtained (Found: Cl = 9·01. Calc., Cl = 9·01 per cent.). Evaporation of the alcoholic filtrate yielded 0·55 gram of lead diethyl chloride (Found: Cl = 21·78. Calc., Cl = 21·09 per cent.).

Action of Thallic Chloride on Lead Diphenyl Di-α-naphthyl.

To a mixture of 1·3 grams of lead diphenyl di-α-naphthyl and 0·65 gram of thallic chloride in 1·7 c.c. of dry ether, 10 c.c. of ether were added, and the whole was heated under reflux for half an hour, and then kept for sixteen hours. The residue, 1·6 grams, after filtering was organic, and contained lead and thallium. It was extracted with 150 c.c. of chloroform, the solution on evaporation yielding 1·0 gram of a crystalline powder (Found: Cl = 7·36. $C_{20}H_{14}ClTl$ requires Cl = 7·39 per cent.). The residue from the chloroform extraction was found still to be a mixture of thallium di-α-naphthyl chloride and lead diphenyl chloride, for by adding

it to boiling concentrated nitric acid the thallium compound was entirely destroyed and, on cooling, crystals of lead diphenyl nitrate separated.

Action of Thallic Chloride on Triphenylphosphine.

A mixture of 1·0 gram of triphenylphosphine and 1·2 grams of thallic chloride in 3 c.c. of dry ether was heated on the water-bath for one hour, then 30 c.c. of benzene were added, and the heating was resumed for a similar period. After filtering, a residue of 0·8 gram of thallous chloride was obtained, and evaporation of the benzene filtrate yielded 0·8 gram of triphenylphosphine (m. p. 78°).

Action of Thallic Chloride on Triphenylarsine.

In the Cold.—To 6·0 grams of triphenylarsine in 30 c.c. of dry ether 6·2 grams of thallic chloride in the same solvent were added. The mixture was well shaken and kept over-night, when a white, amorphous solid separated which, on filtration, was found to be thallous chloride (1·0 gram). Evaporation of the ethereal filtrate caused the separation of a furtber 0·2 gram of thallous chloride, and a viscous, fuming solid remained, from which 5·0 grams of triphenylarsine were recovered (m. p. 57°); the fumes denoted the presence of phenylarsenious dichloride.

In the Hot.—In this case no phenylarsenious dichloride was isolated, but triphenylarsine dichloride, sintering at 158° and melting at 204°, and in addition thallous chloride and thallium diphenyl chloride, together with unchanged triphenylarsine.

Action of Thallic Chloride on 1-Acetoxymercuri-β-naphthol.

To 2·5 grams of the mercury compound 3·88 grams of thallic chloride in 6·4 c.c. of ether were added with shaking. The mixture soon darkened. Twenty c.c. of ether were added, and the whole was heated on the water-bath for fifteen minutes and kept overnight. After filtering, the residue (2·12 grams) consisted of thallous and mercurons chlorides, and evaporation of the filtrate yielded 1·9 grams of tarry product. The latter contained traces of thallic chloride and acetic acid, but neither the tar itself nor alcoholic extractions of it would couple with diazotised aniline solution, and it was concluded that complete disruption of the naphthalene ring had taken place.

Thallium Diphenyl Oxide.

Thallium diphenyl chloride (4·5 grams) and 20 grams of potassium hydroxide in a mixture of 30 c.c. of absolute alcohol and 20 c.c. of

water were heated under reflux for eight hours. The whole was poured into a litre of water, when a white, flocculent mass was obtained, which was filtered and well washed with water. Yield 2·1 grams (Found: Tl = 55·60, 55·81. $C_{24}H_{20}OTl_2$ requires Tl = 55·73 per cent.). The *oxide* is completely soluble in pyridine, colouring the solution pink, is slightly soluble in alcohol or chloroform, and insoluble in water, acetone, xylene, carbon tetrachloride, light petroleum, or ethyl acetate.

Thallium Diphenyl Acetate.—Thallium diphenyl oxide (0·9 gram) was dissolved in 5 c.c. of boiling glacial acetic acid, and the solution was filtered and very slowly evaporated, when 0·43 gram of fine, transparent needles was deposited. Addition of light petroleum to the filtrate gave a further 0·18 gram (Found: Tl = 48·74, 48·83. $C_{14}H_{13}O_2Tl$ requires Tl = 48·91 per cent.). *Thallium diphenyl acetate* melts with considerable gas evolution at 262°, and is completely soluble in hot pyridine, chloroform, toluene, ethyl acetate, or alcohol, moderately soluble in carbon tetrachloride or water, slightly soluble in ether or acetone, and insoluble in light petroleum.

Thallium Diphenyl Nitrate.—Thallium diphenyl bromide (1·0 gram) and 0·42 gram of silver nitrate in 20 c.c. of xylene were boiled for two and a half hours. After filtration, the residue was boiled with water, and with pyridine, the filtrate giving short, transparent needles. Yield 0·68 gram (Found: Tl = 48·28; N = 3·31. $C_{12}H_{10}O_3NTl$ requires Tl = 48·56; N = 3·33 per cent.). The *nitrate* is completely soluble in hot pyridine, very slightly soluble in boiling glacial acetic acid, water, or alcohol, and insoluble in other organic solvents.

Thallium Diphenyl Nitrite.—This was prepared in the way described above, using 1·0 gram of thallium diphenyl bromide and 0·35 gram of silver nitrite, the pyridine solution yielding 0·4 gram of short, transparent needles (Found: Tl = 50·00; N = 3·76. $C_{12}H_{10}O_2NTl$ requires Tl = 50·48; N = 3·47 per cent.). The *nitrite* is completely soluble in hot pyridine, slightly soluble in chloroform or alcohol, very slightly soluble in acetone, and insoluble in other organic solvents.

Thallium Diphenyl Chromate.—The residue obtained by boiling for seven hours 1·0 gram of thallium diphenyl bromide and 0·41 gram of silver chromate in a xylene solution was extracted with pyridine. The filtrate deposited pale yellow, short needles, which burned with slight explosion and did not melt at 290°. Yield 0·56 gram (Found: Tl = 49·17; Cr = 6·21. $C_{24}H_{20}O_4CrTl_2$ requires Tl = 49·03; Cr = 6·25 per cent.). The *chromate* is completely soluble in pyridine, and in boiling glacial acetic acid the yellow colour is destroyed, leaving a white suspension. It is slightly

soluble in acetone and insoluble in water and other organic solvents.

Thallium Diphenyl Pyrophosphate.—This was prepared in the usual manner from 1·1 grams of thallium diphenyl bromide and 0·5 gram of silver pyrophosphate, the mixture being heated for four and a half hours. The residue after filtration was extracted with pyridine and thrown out with ether. Yield 0·4 gram (Found: Tl = 45·79. $C_{24}H_{20}O_7P_2Tl_2$ requires Tl = 45·83 per cent.). The *pyrophosphate crystallises in short, microscopic needles*, which are completely soluble in pyridine, moderately soluble in boiling glacial acetic acid, less soluble in alcohol, ethyl acetate, or chloroform, and insoluble in acetone, ether, carbon tetrachloride, or light petroleum.

Method of Estimation of Thallium and Halogen in Organic Thallium Compounds.

The thallium compound is broken down in a spherical flask (capacity 200 c.c.) having a short ground-glass neck, to which is attached an air-condenser 3 feet long. To 0·2 gram of substance about 20 c.c. of fuming nitric acid are rapidly added and the whole is boiled until it is colourless. The contents of the flask are now washed out and evaporated to dryness, the residue being taken up in water, a few drops of dilute ammonia added, and the thallium precipitated in the hot by means of potassium dichromate. In cases such as the above chromate, the thallium is first removed as thallous iodide, before precipitating the other metal. For the halogen estimation, silver nitrate dissolved in 1 c.c. of water is put in previous to the addition of the fuming nitric acid. The authors find that by this means the haloid is precipitated without loss. After the mixture has been boiled to destroy organic matter, the usual procedure is followed. This method of estimating halogens has given good results in the case of thallium, lead alkyl, and mercury compounds, and would no doubt answer for any type of organic compound which is not explosive with fuming nitric acid, or does not give a stable nitrate, for example, lead diphenyl nitrate, or yield an insoluble oxide, as in the case of tin.

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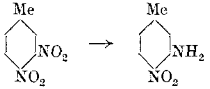
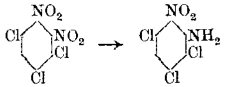
LVIII.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part V. Heteronucleal Dinitro-derivatives.*

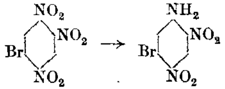
By HAROLD BURTON and JAMES KENNER.

IN the first paper of this series (T., 1914, **105**, 2717), it was suggested that as a corollary to the loosening effect of meta-directive groups on substituents in the ortho- or para-positions, a similar influence of ortho-para-directive atoms or groups on meta-substituents would be observable. At that time, it was only possible to refer to two instances, but since then another has been supplied in the conversion of 3 : 4-dinitrotoluene into 4-nitro-*m*-toluidine rather than into 3-nitro-*p*-toluidine (Kenner and Parkin, T., 1920, **117**, 855) :



Further, the loosening effect of the chlorine atom on nitro-groups in the meta-position to it has been commented on by Hollemann and Hollander (*Rec. trav. chim.*, 1920, **39**, 435). A more detailed discussion of the results of Hollemann and his collaborators will be supplied in a future communication, but the point now under discussion may be illustrated by the case of 3 : 4 : 6-trichloro-1 : 2-dinitrobenzene, from which the 2- rather than the 1-nitro-group is displaced because the effect of the nitro-group in the ortho-position to it is supplemented by those of two meta-chlorine atoms. The 1-nitro-group also has a nitro-group in the ortho-position, but only one chlorine atom in the meta-position relative to it.





Similar considerations at once explain the conversion of 5-bromo-1 : 2 : 4-trinitrobenzene into 5-bromo-2 : 4-dinitroaniline (Giua, *Gazzetta*, 1921, **51**, i, 307). Here the effects of the other three substituents are all to loosen the 1-nitro-group. The alternative possibility would be the replacement of the bromine atom, which has two nitro-groups in suitable orientation to it, but the influence of the third nitro-group is opposed to the change.

This confirmation of the predicted influence of ortho-para-directive substituents is to a certain extent a justification of the reasoning by which it was deduced, and which was based on Flürscheim's substitution hypothesis. These considerations, however, would suggest that ortho-para-directive substituents would also render groups reactive which are attached to the carbon atom to which they are themselves united, and the case of triphenylmethyl chloride lends support to this view (compare T., 1914, **105**, 2719). On the other hand, such induced reactivity would not be anticipated as a result of the attachment of meta-directive groups to a carbon atom. It may therefore appear directly contradictory to these arguments that tetranitromethane and the halogen derivatives of trinitromethane react in alcoholic solution with hydrazine and potassium hydroxide according to the equation (Macbeth and Pratt, T., 1921, **119**, 1356):

$$2XC(NO_2)_3 + 4KOH + N_2H_4 \longrightarrow 2(NO_2)_3CK + 2KX + N_2 + 4H_2O.$$

This displacement of the substituent X leads the investigators mentioned to the conclusion "that a certain parallel may be drawn between the behaviour of the polynitro-aliphatic compounds and polynitro-aromatic substances, especially those in which the ortho-para-influence of the nitro-group exists." This parallel is somewhat limited in character, since, as Macbeth and Pratt point out, in the case of aromatic compounds the formation of substituted phenylhydrazines ensues on the displacement of the reactive substituent:

$$2ArX + 3N_2H_4 \longrightarrow 2Ar{\cdot}NH{\cdot}NH_2 + N_2H_4,2HX.$$

Further, this reaction is equally well carried out in absence of potassium hydroxide (compare, for example, Kenner, T., 1914, **105**, 2732), and it is usually necessary to assist the reaction by warming. Since, in addition, Meisenheimer and Schwartz (*Ber.*, 1906, **39**, 2544) have previously commented on the slight reactivity of the bromine atom in bromotrinitromethane, there is at once ground for the suspicion that the results of Macbeth and Pratt are due to some other cause than that indicated at the beginning of this paper.

This is rendered even more probable by the following considerations. It was shown by Thole and Thorpe (T., 1911, **99**, 2183) that carbethoxy-compounds in general react with sodium ethoxide at the ordinary temperature, losing the carbethoxy-group in the form of ethyl carbonate, if, by so doing, they can acquire a tautomeric hydrogen atom:

$$X{\cdot}CO_2Et + NaOEt \longrightarrow NaX + CO(OEt)_2.$$

This fact, which was subsequently utilised by Thole and Thorpe in the synthesis of various glutaconic esters (*loc. cit.*, p. 2187), is perhaps most simply illustrated by the subsequent work of Scholl and Egerer (*Annalen*, 1913, **397**, 301), who quote, without further comment, the reference to Thole and Thorpe's paper. All previous attempts to prepare alkyl derivatives of ethyl methanetricarboxylate by treatment of its sodium salt with alkyl iodides in alcoholic solution (Conrad and Gutzeit, *Annalen*, 1882, **214**, 35; Michael, *J. pr. Chem.*, 1888, [ii], **27**, 477) had failed, owing, as Scholl and Egerer showed, to the fact that the alkyl derivatives in question are decomposed by sodium ethoxide:

$$CH(CO_2Et)_3 \xrightarrow{RI} R\cdot C(CO_2Et)_3 \xrightarrow{NaOEt} R\cdot C(CO_2Et)\colon C(ONa)\cdot OEt + CO(OEt)_2.$$

The alkyl derivatives are, however, in themselves stable compounds, and obtainable by the reaction indicated, provided that it be carried *out in absence of alcohol*. The same applies to the acyl derivatives and to ethyl methanetetracarboxylate, which are all prepared from the tricarboxylic ester, and at once react with sodium ethoxide, yielding the original ethyl methanetricarboxylate, with, in the case of ethyl acetomethanetricarboxylate, a small amount of ethyl acetomalonate:

$$CH_3\cdot CO_2Et + CH(CO_2Et)_3 \longleftarrow CH_3\cdot CO\cdot C(CO_2Et)_3 \longrightarrow CH_3\cdot CO\cdot CH(CO_2Et)_2 + CO(OEt)_2.$$

Methyl dioxalomalonate is similarly decomposed by ethyl sodiomalonate, and also by water, alcohol, aniline, and phenylhydrazine, although in the last four cases the reaction will readily proceed further if excess of the reagent be employed: *

$$(CO_2R\cdot CO)_2C(CO_2R)_2 \longrightarrow CO_2R\cdot CO_2R + CO_2R\cdot CO\cdot CH(CO_2R)_2$$
$$\downarrow$$
$$CO_2R\cdot CO_2R + CH_2(CO_2R)_2.$$

Since nitroform is a tautomeric compound, it occurred to us that the reaction observed by Macbeth and Pratt might be comparable with those just discussed. An examination of the literature from

* In explanation of the second stage of this reaction, it may be pointed out that ethyl oxalomalonate exists almost entirely in the enolic form (Scholl and Egerer, *loc. cit.*). That this is specially favourable to hydrolysis of the kind observed, seems to follow from the fact that, broadly considered, the analogous "acid hydrolysis" of ethyl acetoacetate and its derivatives is carried out in presence of strong alkali (that is, with the enolic salt), whilst the ketonic hydrolysis occurs when acid or weak alkali is employed, owing to decomposition of the ketonic form.

this point of view then revealed a number of isolated observations, which may all be grouped under an extension of the generalisation already quoted, that compounds which, by the replacement of an atom or radicle by hydrogen, become tautomeric readily undergo this change under the influence of suitable reagents, among which sodium ethoxide and alcoholic potassium hydroxide are the most prominent.

It will be noted that this statement leaves open the questions as to how and why such a change occurs. The following examples, whilst not exhaustive, illustrate, however, its application. Ethyl methyl- (or ethyl-)nitromalonate is converted by sodium ethoxide into ethyl α-nitro-propionate (or -butyrate) (Ulpiani, *Atti R. Accad. Lincei*, 1903, [v], **12**, 441; Hantzsch and Ley, *Ber.*, 1906, **39**, 3155):

$$NO_2\cdot CMe(CO_2Et)_2 \longrightarrow NO_2\cdot CHMe\cdot CO_2Et,$$

and methyl bromonitromalonate into methyl nitromalonate (Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1780):

$$NO_2\cdot CBr(CO_2Me)_2 \longrightarrow NO_2\cdot CH(CO_2Me)_2.$$

Similarly, from dibromonitroacetamide, either dibromonitromethane or bromonitroacetamide is obtained according to the conditions employed (Ratz, *Monatsh.*, 1884, **25**, 725):

$$CHBr_2\cdot NO_2 \longleftarrow NO_2\cdot CBr_2\cdot CO\cdot NH_2 \longrightarrow NO_2\cdot CHBr\cdot CO\cdot NH_2.$$

Dibromo- and chlorobromo-dinitromethanes (Losanitsch, *Ber.*, 1882, **15**, 471; 1883, **16**, 51; 1884, **17**, 848; Schott and Brenneisen, *Ber.*, 1898, **31**, 642), tetranitromethane (Hantzsch and Rinckenberger, *Ber.*, 1899, **32**, 628; Schmidt, Schumacher, and Kuhlmann, *Ber.*, 1921, **54**, [*B*], 1483), trinitroethane (Hantzsch and Rinckenberger, *loc. cit.*), and trichlorobromodinitroethane (E. ter Meer, *Annalen*, 1876, **181**, 1) all behave in the same manner towards alcoholic potassium hydroxide or sodium ethoxide:

$$CBr_2(NO_2)_2 \longrightarrow CHBr(NO_2)_2;$$
$$CClBr(NO_2)_2 \longrightarrow CHCl(NO_2)_2;$$
$$C(NO_2)_4 \longrightarrow CH(NO_2)_3;$$
$$CMe(NO_2)_3 \longrightarrow CHMe(NO_2)_2;$$
$$CCl_3\cdot CBr(NO_2)_2 \longrightarrow CCl_3\cdot CH(NO_2)_2.$$

These examples have been selected in order to show that there is a series of compounds representing a gradual transition from ethyl methanetetracarboxylate to tetranitromethane, which all have this reaction in common, and that therefore the special formulæ for ethyl bromonitromalonate proposed by Willstätter and Hottenroth

(*loc. cit.*), and for tetranitromethane by Schmidt (*Ber.*, 1919, **52**, 400; 1920, **53**, 1529, 1537)

$$(CO_2Et)_2C\overset{O}{\frown}N\cdot OBr;\quad (NO_2)_2C\overset{O}{\frown}N\cdot O\cdot NO_2$$

are, from this point of view at least, unnecessary (compare K. H. Meyer and Wertheimer, *Ber.*, 1914, **47**, 2374), and untenable unless they are extended to ethyl methanetetracarboxylate.*

Phenyldibromonitromethane, which reacts with hydrazine and alcoholic potassium hydroxide according to the general equation already given, is also decomposed by alcoholic potassium hydroxide, with formation of the potassium salt of phenylbromonitromethane (Macbeth and Pratt, *loc. cit.*):

$$C_6H_5\cdot CBr_2\cdot NO_2 \longrightarrow C_6H_5\cdot CBr{:}NO\cdot OK.$$

It must therefore be considered extremely probable that the tendency to acquire a tautomeric hydrogen atom, whatever its cause, is at least contributory to the reactions described by Macbeth and Pratt. When, further, it is noted that, of all the compounds investigated by them, the only one which failed to react, namely, bromonitromethane, was also the only one already provided with a tautomeric hydrogen atom, the conclusion is almost irresistible that this factor determines the reactions observed. The fact that reaction occurs less readily the smaller the number of nitro-groups present corresponds in all probability with a diminution in the tendency of the products of the reaction to assume the *aci*-nitro-form. A rough indication of this is seen in the facts that, whilst nitromethane has no acid properties, dinitromethane in aqueous solution is distinctly acid (Hantzsch and Veit, *Ber.*, 1899, **32**, 610), and that nitroform is one of the strongest organic acids (Hantzsch and Rinckenberger, *loc. cit.*). The tendency to ionisation is, of course, independent of the formation of the *aci*-nitro-form, but this is a necessary preliminary.

It appears, therefore, that the reactions in question do not belong to the same category as those dealt with in the present series of

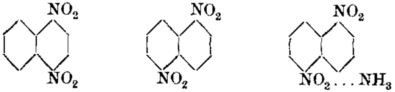
* The formula shown for tetranitromethane is considered necessary to explain the fact that, whilst iodotrinitromethane is entirely converted into the potassium salt of nitroform even by dilute potassium hydroxide solution, tetranitromethane under similar conditions is partly converted into potassium carbonate and potassium nitrate, to an extent which increases with the dilution of the alkali, but does not exceed 33 per cent. (Schmidt, *loc. cit.*). The difference, however, may possibly be due to the more highly unsaturated condition of the carbon atom in tetranitromethane, corresponding with the difference in the smaller demand on its valency made by a nitro-group than by an iodine atom.

papers, and hence that the results they furnish are not directly antagonistic to the views developed herein. A further indication *of the difference is supplied by an observation of Meisenheimer* (*Ber.*, 1903, **36**, 434), who found that, if one molecular proportion *of sodium methoxide be added all at once, instead of gradually, to* trinitroethane, the potassium salt of methyl dinitroethyl ether will *be produced in the same manner as trinitroanisole* is formed from trinitrobenzene:

$$CMe(NO_2)_3 \longrightarrow [OMe{\cdot}CH_2{\cdot}C(NO_2)_3] \longrightarrow OMe{\cdot}CH_2{\cdot}C(NO_2){:}NO{\cdot}OK.$$

The explanation would seem to be that the conditions employed are the most favourable to the exertion by the three nitro-groups of their loosening influence before one of them gives place to a tautomeric hydrogen atom. It remains to be seen whether a similar observation can be made in the case of dinitro-compounds which do not contain a tautomeric hydrogen atom, for example, ββ-dinitropropane. It is probable that in this case reaction will occur less readily, since, as Macbeth and Pratt suggest, and as has been repeatedly emphasised in these papers, the negative character of substituents also contributes to the production of lability. Further evidence of this can now be offered, as a result of experiments made with compounds containing two nitro-groups in different nuclei, but in the same relative positions as in para-compounds.

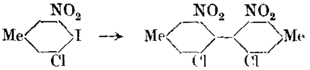
Thus, 1-chloro-4-nitronaphthalene yields 4-nitro-α-naphthylamine when it is heated with alcoholic ammonia, and 1:4-dinitronaphthalene (I), at present unknown, would doubtless behave in a similar manner. 1:5-Dinitronaphthalene (II), however, which contains the nitro-groups in the same relative position, is not attacked by alcoholic ammonia:



(I.) (II.) (III.)

It might possibly be urged that in this case the second nitro-group is not in a suitable position for interaction with the complex grouping of the intermediate molecular compound (III), postulated in such reactions. Such an objection could scarcely, however, apply *to 2:2′-diphenyl derivatives, since it has been shown that the* 2:2′-position corresponds very closely with the ortho-position in *benzene derivatives* (*Kenner and Turner*, T., 1911, **99**, 2101; Kenner, T., 1913, **103**, 613). 2:2′-Dinitrodiphenyl, however, was recovered *unchanged after treatment with alcoholic ammonia.* 2:2′-*Dichloro-*

6 : *6′-dinitro-4 : 4′-ditolyl* (IV), prepared by the action of copper powder on 5-chloro-4-iodo-3-nitrotoluene,



(IV.)

contains a chlorine atom and a methyl group in the meta-position to each nitro-group, which might therefore be expected to make this more mobile than in the case of dinitrodiphenyl itself. Nevertheless, this compound also was unaffected by treatment with alcoholic ammonia. As regards negativity, this compound probably approximates to dinitrodiphenyl, since the influences of the chlorine atom and of the methyl group are opposite in character. It remains to be seen whether the introduction of carboxyl groups ortho- or para- to the nitro-groups will render them mobile, and experiments on the synthesis of such compounds are in progress.

EXPERIMENTAL.

2 : 2′-*Dichloro*-6 : 6′-*dinitro*-4 : 4′-*ditolyl*.

This compound, which was first prepared by Mr. C. W. Judd in collaboration with one of us, results from the gradual addition of copper powder (10 grams) to 5-chloro-4-iodo-3-nitrotoluene (10 grams) at 230°. The mixture is then further heated for one hour at 250° and extracted with benzene. The product, which is also obtained by the action of copper powder on 4 : 5-dichloro-3-nitrotoluene, separates from a mixture of benzene and light petroleum in prisms, m. p. 165° (Found : N = 8·34. $C_{14}H_{10}O_4N_2Cl_2$ requires N = 8·21 per cent.).

Treatment of Dinitro-compounds with Methyl-alcoholic Ammonia.

1 : 5-Dinitronaphthalene (2·18 grams), 2 : 2′-dinitrodiphenyl (2·4 grams), and 2 : 2′-dichloro-6 : 6′-dinitro-4 : 4′-ditolyl (3·41 grams) were separately heated each with ammonia solution (*d* 0·880 ; 4·5 c.c.) and methyl alcohol (32 c.c.) at 150° for sixteen hours, at 200° for sixteen hours, and at 200° for eight hours, respectively. In every case the material was recovered unchanged.

One of us (H. B.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research, which

has enabled him to participate in this work. Further, we wish to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

THE UNIVERSITY,
SHEFFIELD. [*Received, November 17th,* 1921.]

LIX.—*The Composition of Paraffin Wax. Part I.*

By FRANCIS FRANCIS.

THIS investigation was undertaken in the hope that some light might be thrown on the nature of the hydrocarbons contained in paraffin wax. This solid product of the petroleum industry was selected because at temperatures between 130° and 200° it may be more readily oxidised by oxygen-containing gases than the liquid petroleums, and secondly because the process can be carried out, under certain conditions, at a temperature of 100°.

The investigation has now been in progress for some years, and this preliminary account of it describes the first stage of what appears likely to prove a tedious and difficult piece of work.

Since 1918 a series of papers has been published on this subject, but the various authors have only described the results obtained when the oxidation by air or oxygen was carried out at temperatures higher than those I have employed. It is to the use of such temperatures, presumably, that must be ascribed the deep-seated oxidation which takes place, as shown in the number, variety, and relatively low molecular weight of the resulting substances. From such breakdown products, clearly fragments of the original molecular complex, it has not been found possible to obtain any insight into the nature of the hydrocarbons comprising paraffin wax.

I have found, however, that when air oxidation is brought about in the presence of small quantities of turpentine and at temperatures not exceeding 110°, then selective oxidation takes place of one—presumably—class of constituents of the wax, and the resulting derivatives are less numerous than those described by previous observers, and certain members are comparable in molecular magnitude with the hydrocarbons present in the wax. It is believed that these substances are the precursors of the many acids described by other investigators working at higher temperatures.

The part played by turpentine is under investigation, but in the absence of this substance no oxidation has been found to take place with air at 102° in the time occupied by the experiments.

When oxygen is employed instead of air, even at a temperature of 100°, the oxidation appears to proceed further, and among the resulting products, again small in number compared with those described by others, there are present acids of lower molecular magnitude than corresponds with the wax which has been oxidised.

When oxygen is used at the temperature mentioned above, no oxidation takes place until after the lapse of a period in which very considerable change sets in, provided turpentine is present. Oxidation, however, does take place in the absence of this substance, commencing about one month after the wax has been treated continuously with a current of the gas.

A comparison has been made between the oxygen treatment of the wax containing turpentine and the two synthetic normal paraffins—hexadecane, $C_{16}H_{34}$, and dotriacontane, $C_{32}H_{66}$—in the presence of the same substance, but although all the conditions were strictly comparable with the experiments previously mentioned, it was found that no oxidation of these hydrocarbons takes place.

In all the various oxidations which have been carried out with the wax, there is always a residue of unacted-upon hydrocarbons. These hydrocarbons were isolated and re-treated with oxygen, but the resulting material was never found to contain more than a small fraction of the amount of oxygen present when the original wax was treated in a comparable manner.

These observations, together with the previous fact concerning the synthetic paraffins, lead to the conclusion that the method of oxidation employed may be capable of differentiating between what are, probably, normal paraffins, and other at present unknown constituents of the wax which undergo oxidation. This view has been strengthened by the discovery that it is possible to obtain certain fractions, by distilling the wax in a high vacuum, which, under comparable conditions, are very much more readily oxidised than others.

If the interpretation of this observation proves to be correct, namely, that it is possible to separate, or to separate even partly, the wax into oxidisable and non-oxidisable constituents, then the further investigation of the whole problem will be rendered much easier.

I. The Action of Air and Oxygen on Paraffin Wax.

The material used in this investigation was obtained from the Young Paraffin Light Co., Addiewell, and fused between 55° and 56°. Judging from this, from the analytical data, and from the molecular-weight determination carried out by the ebullioscopic method

using benzene as solvent—all given in Table I, experiment 1—the substance appeared to consist of hydrocarbons corresponding closely with the average analysis of such paraffin waxes, namely, C = 85·15; H = 14·85 per cent. Our knowledge, however, is insufficient for any statement to be made as regards the nature of these hydrocarbons, although they are generally supposed to be mixtures of normal members of the paraffin series.

When a rapid current of dry air, free from carbon dioxide, was passed through the molten wax at a temperature of 70—80°, no oxidation was found to take place in one hundred and sixty-eight hours, and at 90° there was no change in three hundred and thirty-six hours.

In the next experiments, numbered 2 and 3 in Table I, analytical data are given for the resulting material. These were carried out at higher temperatures than the above, but under precisely the same conditions, in the same thermostat, and at the same time as those to be described later, in which small quantities of turpentine were present in the molten wax.

The results obtained with oxygen, passed through the wax by means of fine jets, are also given in the same table, and these may be compared with the analyses of the resulting material when turpentine is present (see Table II).

TABLE I.

Expt.	M. p.	Mol. wt. Ebullioscopic method in benzene.	Iodine value.	Temp.	Air current. Duration in hours.	Analysis. C.	H.	O, by difference.
1.	55–56°	363–366	3·9			85·4	14·7	—
2.	55–56	360		101–103°	333	85·4	14·6	—
3.	56–57	—	3·9	110	282	85·3	14·6	—
					Oxygen current.			
4.	55			100	240	85·1	14·8	—
	53–55		3·08	,,	696	85·4	14·4	—
	50–54		3·39	,,	862	84·9	14·5	0·6
	46–52		3·71	,,	956	82·2	14·0	3·8
	36–46		—		1276	74·7	11·6	13·7

The data in Table I show that the wax is not attacked by air during two hundred and eighty hours at 110° or by oxygen during seven hundred hours at 100°.

In the case of oxygen, the sudden increase in the velocity of oxidation after the lapse of so long a period is interesting, and it is highly probable that if the experiments with air had been continued for a sufficient length of time similar results might have been

obtained. Judging from the iodine values, there is no indication of the formation of unsaturated substances previous to the onset of oxidation. Oxidation commences, as it does in all cases investigated, with the simultaneous formation of water, carbon dioxide, and formic acid.

A further communication on what may be termed the latent period in the oxidation will be published shortly. It may be stated here, however, that when paraffin wax is kept in a vacuum at 100° for seven hundred hours, and afterwards treated with a current of oxygen, this period is diminished by about 20 per cent.

That oxidation takes place readily, with varying degrees of velocity, at higher temperatures has been determined by many investigators.

Besides various patents dealing with the oxidation of paraffin wax by air at temperatures between 120° and 150°, of which the first is that taken out by Schaal in 1884, the following are of importance—Bergmann (*Z. angew. Chem.*, 1918, **31**, 69, 115, 148) has used air at 130—135°; Kelber (*Ber.*, 1920, **53**, [*B*], 66, 1567) at 140—150°, and states that with oxygen the reaction becomes violent if the temperature rises above 200°, but at such temperatures it will be complete in four to five hours. Fischer and Schneider (*Ber.*, 1920, **53**, [*B*], 922) used temperatures 135—145° and up to 170°, and also carried out the process under pressure. Grün (*Ber.*, 1920, **53**, [*B*], 987) states that paraffin wax can be oxidised in four to five hours with oxygen at 130—135° and that the composition of the resulting material depends on the temperature employed and on the duration of the experiment. Löffl (*Seifen Z.*, 1920, **27**, 622) also mentions the importance of temperature and states that the best yield of acids is obtained at 115—120° under three atmospheres' pressure. Franck and others have also used oxygen at a temperature of 150°.

It is certain that oxidation with either air or oxygen can be brought about readily at temperatures above 130°, although the experiments described in Table I indicate unquestionably that, at the temperatures described and in the time stated, oxidation either does not take place, or does so with such a small velocity that after the lapse of a considerable period the amount of oxygen in the resulting product is incapable of detection from the results of carbon and hydrogen analyses.

The discussion of the relatively low molecular weight products obtained by the above investigators is left to a future communication.

The very large increase in the velocity of oxidation when the process is carried out in the presence of small quantities of turpentine is described in the next section, and this reaction was

under investigation before any of the papers mentioned above had been published.

II. The Action of Air and Oxygen on Paraffin Wax containing Turpentine.

When a small quantity of turpentine is added to the wax and the resulting material treated with a current of air or oxygen under precisely similar conditions to those previously described for the wax alone, then oxidation does take place.

In experiments numbered 2A and 3A, Table II, the current of air passed first through molten paraffin—the analyses of the resulting materials are given in experiments 2 and 3, Table I—then througb a layer of cotton wool to retain the wax carried over as vapour by the air current, and amounting to 1·5 per cent. of the whole material in three hundred and thirty-three hours, and finally into another quantity of the wax containing 5 per cent. of turpentine. The analytical data for the resulting material from a series of such experiments with air and oxygen are given in Table II.

In experiments 2A, 3A, 4, and 5, the results of which are summarised in Table II, a considerable amount of turpentine was carried away by the air current. It was collected in tubes filled with cotton wool, and in experiment 4 the amount of unchanged material obtained showed that the oxidation could have been effected witb considerably less than the 5 per cent. of turpentine actually employed.

In the case of oxygen, the gas stream carried over but very small quantities of volatile material, which in these cases condensed in the cool part of the reaction vessel.

The results given in Tables I and II illustrate the following deductions :

(1) Paraffin wax treated with dry air at 101—103° for three hundred and thirty-three hours is not affected, whereas in the presence of 5 per cent. of turpentine the resulting material contains 10·8 per cent. of oxygen.

(2) Treated with oxygen at 100° for six hundred and ninety-six hours, paraffin wax is not oxidised; but in the presence of 5 per cent. of turpentine the resulting substance contains 19.per cent. of oxygen.

(3) The velocity of the reaction with oxygen is greater than with air, although the temperature is lower; also the oxidation proceeds further.

(4) In the oxidation with oxygen using turpentine (experiment 6, Table II) the process appears to cease after the lapse of six hundred and ninety-six hours, since the product contains the same percentage

TABLE II.

Expt.	Remarks.	Rapid current of dry air, free from CO_2. Temp.	Duration in hours.	M. p.	Analysis. C.	H.	O, by difference.
2A	400 Grams of paraffin wax and 20 grams of turpentine.	101–103°	333		76·6	12·6	10·8
3A	,, ,,	110	282		77·7	12·6	9·7
4	1000 Grams of paraffin wax and 50 grams of turpentine.	109–110	646		78·3	12·7	9·0
5	100 Grams of paraffin wax and 5 grams of turpentine.	100	595	46°	78·3	12·8	8·9
		Dry oxygen from fine capillaries.					
6	,, ,,	100	48	52–52	85·2	14·3	0·5
		,,	144	47–49	83·7	14·5	1·8
		,,	192	47–49	83·0	14·0	3·0
		,,	240	44–48	82·3	13·5	4·2
		,,	312	44–48	79·9	13·3	6·8
		,,	360	43–47	78·7	13·1	8·2
		,,	408	40–45	78·8	12·7	8·5
		,,	480	37–43	76·1	12·4	11·5
		,,	600	34–40	73·4	11·6	15·0
		,,	696	35–41	70·2	10·8	19·0
		,,	936	39–43	70·3	10·7	19·0
		Air saturated with moisture.					
7	,, ,,	100	501	53–55	84·8	14·5	0·7
		Dry oxygen.					
8	*Dotriacontane and 5% of turpentine.*	100	696		85·0	15·1	
			before treatment		85·0	14·9	
9	Hexadecane and 5% of turpentine.	,,	260		84·4	14·7	0·9
			730		84·4	15·3	
				calculated	85·0	15·0	

of oxygen after a further two hundred and thirty hours' treatment with this gas. It will be noticed, however, that the melting point of the resulting material, which falls gradually for the first six hundred hours, commences to rise after that period. It is believed that this has a bearing on the nature of the resulting acids.

(5) Moisture appears to inhibit the oxidation process. After five hundred and ninety-six hours' treatment with dry air the product contains 9 per cent. of oxygen, but in the case of moist air only

0·7 per cent. after five hundred and one hours. Although moisture appears to act in this manner, yet if the reaction has actually commenced it does not hinder its progress.

(6) The two synthetic hydrocarbons, dotriacontane and hexadecane, are not oxidised under the conditions described. As will be seen later, there are constituents of paraffin wax which do not appear to be oxidised by the method employed.

III. Minor Products of the Oxidation, and the Action of Turpentine.

(*A*) In all cases when oxidation takes place, water, carbon dioxide, and formic acid are evolved. That this is due, in part at least, to the oxidation of turpentine is certain, but that it is not entirely the case is shown by the fact that these substances are also formed after prolonged treatment of paraffin wax with oxygen in the absence of that substance.

In experiment 4, Table II, in which 1 kilo. of wax was oxidised, carbon dioxide was slowly evolved during the process, although it practically ceased forty-eight hours before the air current was stopped. By allowing the air current to pass through a series of wash-bottles containing an excess of barium hydroxide solution, 60 grams of barium carbonate, corresponding with 13·5 grams of carbon dioxide, were collected and the volatile acids were converted into barium salts, of which 50 grams were obtained. An analysis of these salts, and an investigation of the acids obtained from them, showed that they consisted of more than 80 per cent. of formic acid, of which consequently about 17 grams had been formed in the reaction.

These minor products of oxidation may be of significance, but their bearing cannot be discussed until further knowledge of the process shall have been obtained.

(*B*) In the above experiment, a total amount of 100 grams of turpentine was used, and there was carried over by the air current and collected in the manner described, 102 grams of a liquid consisting of about 40 grams of unchanged turpentine, 45 grams of a liquid of a higher boiling point, which is similar to the material formed when turpentine itself is treated with air, and 9—10 grams of a liquid acid. It is clear that it is possible to account for a very considerable amount of the turpentine used in the process.

Although the acid mentioned above may contain small quantities of substances derived from turpentine, its close analogy with that obtained from the oxidation of paraffin wax in the absence of that material shows that it belongs to what we have provisionally classified as the " γ " acids, which will be discussed later.

That the velocity of the oxidation of paraffin wax is greatly accelerated in the presence of turpentine is clear, and that this substance itself suffers change during the process has also been established. The action of air and oxygen on turpentine is now being investigated, and the results obtained up to the present with air support the views expressed concerning this substance.

A consideration of the relationship between the amount of oxygen present in the final product (Table II, No. 6) and the duration of the oxygen current, points to the possibility that the process is one of auto-oxidation; but with the information at present at our disposal it is not possible to discuss the part played by turpentine in bringing about the oxidation.

IV. Investigation of the Products of Air Oxidation.

The products of the oxidation fall into two groups:

(*A*) The small quantities of volatile materials, water, carbon dioxide, and formic acid, carried over by the air current and described in the previons section.

(*B*) The substances remaining in the reaction flask and composed of:

i. Small quantities of acidic material of low molecular weight, mentioned in the previous section, and amonnting to between 2 and 3 per cent. in all.
ii. Acidic substances of molecular weight corresponding with that of the paraffin oxidised.
iii. Non-acidic oxidised material and unacted-upon hydrocarbons.

The oxidised paraffin, when solid, resembles bees'-wax. After many attempts to treat this material in such a manner as to effect a separation of acidic from unchanged wax and non-acidic oxidised material, the most satisfactory method that was found consisted in dissolving 100 grams of the molten product in 400 c.c. of absolute alcohol, adding 10 c.c. of 40 per cent. sodium hydroxide solution to the hot liquid, and then slowly pouring into this solution 200—250 c.c. of hot water. Two layers were formed and could be separated by means of a syphon. The upper layer, *solidifying on cooling*, consisted of the wax and inert oxidised material; the lower of a solution of alkaline salts, which on acidification gave a dark-coloured oil, solidifying on cooling. The acidic and non-acidic fractions were repeatedly washed with boiling water and dried at 90° in a vacuum before analysis.

Table III gives the analytical data for various preparations of acidic and non-acidic material obtained by employing the above method.

A comparison of the analyses, given in Table III, of the various preparations of acidic and non-acidic materials, shows that the method of separation is better than might have been expected; but it is one that requires some experience in order to avoid the formation of emulsions.

The alkaline salts of the acidic material carry into solution varying amounts of non-acidic substances, and give rise to a slightly opalescent, soapy solution which cannot be extracted by any of the ordinary organic solvents, owing to the formation of emulsions. On acidification, the total material present is thrown out of solution, and the formation of various mixtures of acidic and non-acidic substances accounts for the differences in acid values obtained, and magnifies the yield given in column 5 in a manner that will be discussed later.

Further, the separation is one that does not lend itself to great accuracy, and the numbers in column 5, with the possible exception of experiment 4A, can be regarded only as approximations correct to about 3 per cent.

When the mixture of solid acids described above has been separated by *acidification of the aqueous alcoholic solution (and their* solubility in this medium was found to be extremely small), the solution still contains small quantities of soluble acids, which amounted to 22 grams in the case of the experiment in which 1 kilo. of paraffin wax was oxidised. These appear to be identical with the material carried over by the air current, amounting to 9 grams and described in section III. This acid gave the following data on analysis: C = 59·86; H = 8·44; O = 31·70 per cent.; the molecular weight by the ebullioscopic method using acetone as solvent was 202, and the acid value 309. For the sake of future reference these acids have been placed in the "γ" group, and they will be discussed later.

Up to this point, taking the data from the experiment carried out with 1 kilo. of paraffin wax, the composition of the material in the reaction flask is 39 per cent. of non-acidic substances composed of unchanged constituents of the wax and oxidised hydrocarbons; 59 per cent. of impure acids containing oxidised hydrocarbons and small amounts of unchanged hydrocarbons; and in all about 3 per cent. of "γ" acids.

TABLE III.

Acidic Material B. ii.

Expt.	Remarks.	Dry air current. Temp.	Dry air current. Duration in hours.	Yield of crude acidic substances per cent.	Mol. wt. Ebullioscopic method using acetone.	M. p.	Acid value.	Analysis. C.	Analysis. H.	Analysis. O, by difference.
2B	Oxidation of 40 grams.	101–103°	168	12						
			333	25		42–43°	120	74·1	11·8	14·1
3B	Oxidation of 400 grams.	110	282	56		41–42	112	74·4	11·4	14·2
4A	Oxidation of 1000 grams.	109–110	646	59	440	42–45	75	74·9	11·9	13·2
7		96–98	336	60	446	41–42	123	74·4	11·2	14·4
8		104	168	60	436	40–41	123	73·3	11·5	15·2
9	Residual hydrocarbons from previous oxidations.	106–110	261	14	—	42–48	88	76·0	12·1	11·9
10	800 Grams of material from various preparations, used in the present investigation.	—	—	—	442	40–42	82·6	75·2	11·9	12·9

Non-acidic Material B. iii.

Expt.	Source.					M. p.	Acid value.	C.	H.	O, by difference.
4B	Residue from the oxidation of 1 kilo. of paraffin wax (4A above).		—	—	—	47–50	1·2	80·5	13·4	6·1
11	Collection of residues from 2B and 3B above.		—	—	—	45–52	0·8	81·4	13·7	4·9
12	Residue from No. 9 above.		—	—	—	49–53	0·6	81·3	13·6	5·1

V. Investigation of Acidic Substances from Air Oxidations.

[With JOHN CLIFFORD POPE.]

Owing to decomposition it was not found possible to separate the constituents of this mixture by fractional distillation in a vacuum. This, and the impossibility of recrystallising the material, added greatly to the difficulties in the way of, first, separating the acidic from the non-acidic constituent which was known to be present in the material resulting from the preliminary separation, mentioned in section II, and still further of separating the mixture of acidic substances themselves. It was only after a considerable amount of work had been carried out that the former was accomplished. The results of the latter will be communicated at a later date.

(*A*) The crude acidic material gives sodium or potassium salts from which the inert material present cannot be extracted by the ordinary solvents. The analyses of the acids from different specimens of barium salts washed with light petroleum by different methods are given in Table IV, C, D, I, J.

(*B*) The analysis of the acid obtained from the most soluble fraction of the magnesium salts in ethyl alcohol is given in Table IV, E.

(*C*) A more satisfactory method of separating the constituents of the mixture consists in pouring the molten material into ten times its weight of ethyl alcohol containing 8 per cent. of water. The characteristics of the more soluble fraction are given in Table IV, experiment F.

(*D*) It was only at a later stage of the investigation that it was found possible to separate readily such mixtures of acidic and inert material by dissolving them in a mixture of 50 per cent. of alcohol and 50 per cent. of water containing an excess of sodium hydroxide, and repeatedly extracting the solution with light petroleum. By this method the formation of emulsions is entirely avoided, and a very satisfactory separation into acidic and non-acidic substances soluble in the solvent can be effected.

Various fractions obtained from the original mixture by treatment with alcohol as described in this section (No. *C*) were subjected to this process of separation, and the analyses of the acids obtained from the more soluble fraction are given in Table IV, experiments G and H.

The acids, freed from inert material by this method, were then converted into barium salts, which were extracted with light petroleum. The analyses of the acids obtained from the insoluble

(experiment K) and soluble barium salts (experiment L) are given in Table IV.

For the sake of reference, we term the substances from the *soluble* barium salt the "α"-acids, those from the *insoluble*, the "β"-acids.

TABLE IV.

Expt.	Source of acid (air oxidation).	Mol. wt. Ebullioscopic method with acetone as solvent.	M. p.	Acid value.	Analysis. C.	H.	O, by difference.
C	Barium salt (Soxhlet) from crude acids.		47–49°	149	73·5	11·6	14·9
D	Barium salt from crude acids.		44–45	131	73·0	11·6	15·4
E	From magnesium salts.	406	37	114	73·6	11·4	15·0
F	Soluble in 92% alcohol.		35	110	73·8	11·4	14·8
G	Separation by light petroleum; lowest m. p.	410	37·5	137	72·8	11·3	15·9
H	Separation by light petroleum; second fraction.	400	43	138	73·3	11·5	15·2
I	Barium salt insoluble in light petroleum.	410	42	154	74·0	11·9	14·1
J	Barium salt soluble in light petroleum.		9–10	89	73·6	11·0	15·4
K	Barium salt, insoluble in light petroleum, from acids free from inert material.	326	43·5		73·0	12·1	14·9
L	Barium salt, soluble in light petroleum, from acids free from inert material.	452	liquid	141	72·1	11·2	16·7

The method of separation described in this section (No. D) shows that the crude acids (see column 5, Table III) are composed of 54 per cent. of acids and 46 per cent. of non-acidic material.

VI. Non-acidic Substances from Air Oxidation.

(*A*) The non-acidic substances separated as described in section IV are seen by reference to Table III to contain between 5 and 6 per cent. of oxygen. This mixture of inert oxidised material and unchanged hydrocarbons of the paraffin wax is very difficult to separate by fractional distillation in a high vacuum.

(*B*) The crude acidic substances are seen by reference to Table III

to contain an average of about 13·8 per cent. of oxygen, whereas the purer material (see Table IV) contains between 14 and 15 per cent. This is due, as previously indicated, to the fact that the alkaline salts, from which they were obtained, are capable of carrying into aqueous solution a considerable amount of inert oxidised material and what is believed to be smaller quantities of unchanged hydrocarbons.

(1) The complete separation of the oxidised non-acid fraction (see Table III, B iii) from the non-acidic mixture containing hydrocarbons is a difficult matter. The method we have adopted consists in dissolving the mixture in boiling acetone, when, on cooling, the majority of the hydrocarbon crystallises out, but only an impure oxidised material containing 7·8 per cent. of oxygen can be obtained from the solvent.

During this separation a small amount of a substance was isolated practically insoluble in acetone. It showed an extremely high molecular weight, but as it amounted only to about 1·5 per cent. of the whole material, it has not been investigated further.

(2) A mnch purer specimen of the non-acidic substance can be obtained from the crude acidic material (see table III, B ii) on treatment with alcohol, as described in section V, No. C. When the fractions are further purified as described in section V, No. D, the non-acidic constituent can be isolated from the light petroleum used. The analysis of two specimens, 1 and 2, isolated in this manner from the two most soluble fractions, are given below.

The purest preparations, small in amount but presumably free from hydrocarbons, were obtained in the case of No. 3 from the material extracted by light petrolenm from the barium salts (see Table IV, K and L) and in that of No. 4 during the separation of the acids by means of their lead salts.

			Analysis.		
	M. p.	Mol. wt. Ebullio-scopic method.	C.	H.	O, by differ-ence.
1.	Inert oxidised semi-solid	375	77·3	12·5	10·2
2.	,, ,, ,,	380	77·1	12·7	10·2
3.	,, ,, liquid	—	74·9	11·9	13·2
4.	,, ,, ,,	—	75·2	12·1	12·7

As far as the investigation has progressed at present we are now in a position to state the approximate composition of the solid material resulting from the passage of air through paraffin wax in the presence of turpentine and under the conditions mentioned. The data are given in Table V.

TABLE V.

	Per cent.
Acids designated α and β, together ...	32
„ „ γ, about ...	2·5
Inert oxidised hydrocarbons, containing 10 per cent. of oxygen ...	10
Hydrocarbons, m. p. 55–64° ...	19
Material of high molecular weight, about ...	1·5
Mixture of hydrocarbons and non-acidic oxidised material containing 3–4 per cent. of oxygen ...	16
Mixture similar to above but containing 7–8 per cent. of oxygen	17

On the supposition that the inert oxidised material contains 13 per cent. of oxygen, the total amount present is 22 per cent., and unchanged hydrocarbons 40 per cent.

VII. Separation of Products of Oxidation with Oxygen in the Presence of Turpentine.

The course of the oxidation can be estimated from the data given in Table II, experiment 6. As in the previous oxidation with air, there was 5 per cent. of turpentine present, and the process was carried out in a steam-bath.

It is unnecessary to give any details of the methods employed to effect the separation of acidic and non-acidic substances; it was readily carried out by extracting the aqueous alcoholic solution of the sodium salts with light petroleum. This process was rendered easier owing to the fact that the oxidations had proceeded further and there were less unacted-upon hydrocarbons present. The data are given in Table VI.

TABLE VI.

Oxidation with Oxygen. Temperature = 100°. Turpentine present.

	Per cent.	M. p.	Acid value.	Mol. wt. Ebullioscopic method with acetone as solvent.	Analysis. C.	H.	O.
Crude material from reaction vessel.		39–43°	149	—	70·3	10·7	19·0
Solid acids β	47	43	188	331	71·5	11·3	17·2
Liquid „ γ	7		392	—	61·7	9·0	29·3
„ „ δ	14		—	—	54·6	7·8	37·6
Non-acidic	25	47	1·1	393	80·7	13·5	5·8
	Estimated %						
Non-acidic acetone separation: Hydrocarbons	15	57·5	—	—	84·2	14·2	1·6
Non-acidic acetone separation: oxidised	10	27	—	—	77·4	12·7	9·9

It appears from the above table that oxygen at 100° brings about a much more profound oxidation than in the case of air at 110°. The β-acids formed, probably containing small quantities of α-acids, amount to 47 per cent. compared with 32 per cent. of α- and β- in the case of air. Further, the γ-acids are formed to the extent of 7 per cent. as compared with between 2 and 3 per cent. in the case of air, and in addition there is also present 14 per cent. of acids with yet smaller carbon content. As regards the inert oxidised material, 10 per cent. is formed compared with 22 per cent. when air is used, and a very much smaller amount of hydrocarbons remains unoxidised.

VIII. Products of Oxidation with Oxygen in the Absence of Turpentine.

As stated in section I, the oxidation of paraffin wax with oxygen appears to set in rapidly after the lapse of about seven hundred hours (see Table I, experiment 4). The resulting oxidised material was separated into acidic and non-acidic constituents by the method previously described. The data are given in Table VII.

TABLE VII.

Oxidation with Oxygen. Temperature = 100°. Turpentine absent.

	Per cent.	M. p.	Acid value.	Mol. wt. Ebullioscopic method with acetone as solvent.	Analysis. C.	H.	O.
Solid acids β	38	47°	200	318	71·7	11·9	16·4
Liquid ,, γ	8		367		62·7	9·4	27·9
,, ,, δ	9						
Non-acidic	42	49·5	0	390	82·7	14·0	3·3

From the lower oxygen content and higher melting point of the neutral material, it is clear that this fraction contains a higher percentage of hydrocarbons than when turpentine is present during the oxidation.

The amount of solid acids is also lower, and it is presumed that the reaction had not progressed as far as in the previous oxidation (section VII). We point out here that the presence of the acids termed γ and δ indicates that these are derived, certainly in this case, from paraffin wax; but when turpentine is used it is possible that derivatives formed from this substance may also be present in small amounts in those acids.

IX. Classification of Acids formed in Oxidation Processes.

For the sake of future reference we have classified the acids isolated in this investigation into four groups, α to δ. We do not attempt to formulate any of these substances, since it is almost certain that none of them is pure. The data given serve, as they have served throughout this investigation, merely as a guide to the work we are carrying out.

The α- and β-acids are the main acidic products of *air oxidation,* and an inspection of the analytical data in Table IV, experiments D to H, shows that the composition of the mixture varies but little from the mean values C = 73·3; H = 11·4; O = 15·2 per cent. This mixture is very insoluble in water or mixtures of water and alcohol, and shows a mean molecular weight of about 408.

By the method we have described it has been found possible to separate this mixture into an acid (or acids) of low melting point and high molecular magnitude, which we have termed the α-acids, and those generally of higher melting point and smaller molecular weight, termed the β-acids. The solid β- and liquid γ-acids of higher acid value are the main acidic oxidation products when oxygen is employed.

The γ-acids are liquids slightly soluble in aqueous alcohol, and the δ-acids are soluble to a considerable extent in water, but the latter acids, isolated only in small amounts, have so far not been further investigated.

There is no doubt that the α- and β-acids, constituting 32 per cent. of the total oxidation mixture (Table V) when air is used, and the β-acids (with much smaller quantities of α-) forming 47 per cent. when oxygen is employed (Table VI), are the most interesting acidic products of the reaction. It has been found possible to isolate from these mixtures well-defined acids by means of the relative solubility of their lead salts in alcohol. By this means the α-acids have been further purified, and the β-acids have been separated into at least four constituents.

X. Nature of Unoxidised Hydrocarbons.

[With REGINALD HENRY COYSH.]

The inert material which had been twice oxidised and the analyses of which are given in Table III, experiment 11, was separated by solution in acetone, and the resulting hydrocarbon purified by distillation in a vacuum of 0·5 mm. (see section VI, B). This hydrocarbon in the presence of 5 per cent. of turpentine was then treated

as previously described, with a current of oxygen at 100°. After the gas had passed for six hundred and seventy-two hours, the analysis showed the presence of 6·4 per cent. of oxygen. Had the original paraffin wax been employed, the amount of oxygen in the resulting material would have been 18 per cent.

We concluded that the previous treatments with air had freed the paraffin wax from most of its oxidisable constituents, and the resulting hydrocarbons were composed of materials which are either not oxidised by the treatment described or are oxidised only with a very small velocity. We attempted to isolate the oxidisable constituents by a partial fractional distillation of the original paraffin wax in a vacuum of 0·5 mm.; of the fractions obtained four were selected and treated with oxygen in the presenee of 5 per eent. of turpentine at 100° under strictly comparable conditions. The data are given in Table VIII, where the percentage of oxygen is determined by difference from earbon and hydrogen analyses.

TABLE VIII.

Oxidation of Certain Fractions, from Paraffin Wax, with Oxygen. Temperature = 100°.

Fraction.	No. 1.		No. 2.		No. 3.		No. 4.	
B. p. at 0·5 mm.	170–180°		190–200°		205–220°		Residue, above 232°.	
M. p.	41–43		51–52·5		56·9–57·2		64–64·7	
Mol. wt. Ebullioscopic method using benzene.	292		—		—		423	
Duration of oxygen current in hours.	M. p.	%O.	M. p.	%O.	M. p.	%O.	M. p.	%O.
123	41–43°	0·3	48–51°	0·6	54–57°	2·9	64–64·7°	
268	41–42	1·9	41–45	5·3	46–52	6·0	62–65	1·0
435	41–42	4·0	38–46	12·2	45–52	8·9	61–64	2·6
720	36–40	4·5	38–43	15·2	44–51	12·0	60–63	3·2

It will be seen from the above table that whereas the fractions used in the experiments boiling between 170° and 180°, and that above 232°, contain in the resulting material only between 3 and 4·5 per cent. of oxygen, that boiling between 190° and 200° contains 15 per cent., and that between 205° and 220°, 12 per cent. of oxygen. We have no doubt that there is present in that fraction of wax which we found to distil between 190° and 220° the largest proportion of those constituents of paraffin wax oxidisable by the method employed in this investigation.

We regard these results as so satisfactory that we are now engaged in isolating the oxidisable hydrocarbons by a much more complete

fractional distillation of the paraffin wax in a vacuum of 0·1—0·15 mm. Besides being of great interest in themselves, such substances will serve as a more convenient material for the further investigation of the general problem.

Our thanks are due to the University Colston Society for grants towards the expenses of this work, and to the Department of Scientific and Industrial Research for assistance which enabled one of the authors (J. C. P.) to take part in the investigation.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL. [Received, December 19th, 1921.]

LX.—*The Formation and Stability of* spiro-*Compounds. Part VII. The Application of the Dieckmann Reaction to Esters of the Glutaric Series.*

By GEORGE ARMAND ROBERT KON.

IN Part IV of this series (Kon, T., 1921, **119**, 810), it was pointed out that glutaric acid does not give rise to compounds of the *cyclo*butane series by Wislicenus's or Dieckmann's reactions, apparently because the acetic residues in this acid are too far apart to interact in the required manner. It was shown that by introducing a *gem*-grouping or ring into the chain in the β-position it was possible to cause a convergence of the acetic residues (*loc. cit.*, p. 812), and that acids substituted in this way could be made to undergo Wislicenus's reaction, although the cyclic ketones primarily formed were found to isomerise to unsaturated ketones.

The tendency to pass into a cyclic ketone which a given acid should possess was expressed mathematically in the form of "formation numbers" by Dr. C. K. Ingold (see his note to the author's paper, *loc. cit.*, p. 816), and it was shown that the acids studied formed a series connecting the glutaric with the adipic series of dicarboxylic acids as regards their tendency to pass into cyclic ketones.

An attempt was made to establish a "critical formation number" for the production of cyclic ketones by the Wislicenus reaction, and it was concluded that this figure lay somewhere in the region between the figures 0·43 (for glutaric acid) and 0·38 (for ββ-dimethylglutaric acid); the critical "figure of instability," on the other

hand, could not be ascertained because in all cases the cyclic ketone underwent isomerisation.

It appeared of great interest to study the application of another classical reaction to the same series of acids. This reaction is that elaborated by Dieckmann (*Ber.*, 1894, **27**, 102; *Annalen*, 1901, **317**, 27) and consists in the elimination of alcohol from the ester of a suitable dibasic acid:

$$(CH_2)_n<\begin{matrix}CH_2\cdot CO_2R\\ CH_2\cdot CO_2R\end{matrix} \xrightarrow{Na}$$

$$(CH_2)_n<\begin{matrix}CH_2\\ CH(CO_2R)\end{matrix}>CO \xrightarrow{\text{hydrolysis}} (CH_2)_n<\begin{matrix}CH_2\\ CH_2\end{matrix}>CO$$

The formation numbers of the ketonic esters are identical with those of the corresponding ketones (*loc. cit.*, p. 818). The calculation of their figures of instability is attended with difficulty, but it is plain on general grounds that they must show the same mutual relationship as those given for the ketones (*loc. cit.*, p. 817), and it therefore follows that of the esters investigated it is the *cyclo*hexane compound which should be the most easily formed and the most stable. It may be stated at once that this conclusion is fully borne out by experiment.

The action of sodium on ethyl glutarate has already been studied by Dieckmann himself (*Annalen*, 1901, **317**, 27), who succeeded in obtaining a very small amount of oil insoluble in aqueous sodium carbonate and giving a blue colour with alcoholic ferric chloride. He was unable to investigate it further or to obtain the expected *cyclo*butanone from it on hydrolysis.

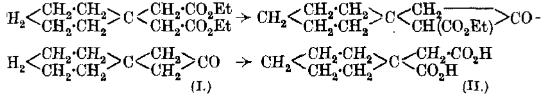
Dieckmann's experiments were therefore repeated, and extended to the esters of three other acids, namely, ββ-dimethylglutaric, *cyclo*pentane-, and *cyclo*hexane-diacetic acids, sodium and potassium being used as condensing agents under comparable conditions.

The difference in the behaviour of the last-named three esters from the first one was most marked.

Ethyl glutarate readily reacts with sodium or potassium, but on working up the product it is found that the substance formed consists entirely of an extremely viscous gum, completely soluble in aqueous sodium hydrogen carbonate, although insoluble both in ether and in water. So far all attempts to isolate a pure compound from this substance have failed.

The action of potassium (or sodium) on the other three esters, on the other hand, gives rise to definite and well-characterised products, and it will be shown later that their formation is originally due to the production of a cyclic ketonic ester. Such a ketonic ester has in no case been isolated, but in the experiments with ethyl

*cyclo*hexanediacetate it was possible to isolate the cyclic ketone derived from the ester by the loss (by hydrolysis) of a carbethoxyl group, namely *cyclo*hexane*spirocyclo*butanone (I), the constitution of which is placed beyond doubt by its oxidation to *cyclo*hexane-1-carboxylic-1-acetic acid (II).



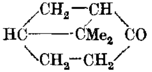
(I.) (II.)

This remarkable substance is analogous to *cyclo*hexane*spirocyclo*propanone, which was obtained in the form of its semicarbazone by Beesley, Ingold, and Thorpe (T., 1915, **107**, 1080). The quantity prepared by them was, unfortunately, too small to allow the isolation of the ketone itself.

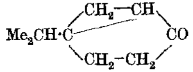
The yield of the new ketone is also very poor, barely reaching 1 per cent. of the theoretical, and it has therefore only been possible to study the most important properties of the substance.

The ketone is saturated, being quite stable to neutral permanganate, and is only slowly attacked by the alkaline reagent in the cold.

The optical properties of the substance were determined, and it was found that there was a marked exaltation in the molecular refraction (+ 0·77) and also in the dispersion. A similar exaltation due to the presence of the *cyclo*butane ring is observed in the isomeric nopinone (III) (+ 0·57) (Oestling, T., 1912, **101**, 457); the increase is not, however, as great as in the case of sabina ketone (IV), which contains a *cyclo*propane ring (+ 0·96) (Wallach, *Annalen*, 1907, **359**, 265).



(III.)



(IV.)

In addition to the ketone (I) and unchanged *cyclo*hexanediacetic ester, as well as *cyclo*hexanediacetic acid resulting from the hydrolysis *of the ester, a solid diketone,* $C_{10}H_{14}O_2$, *is formed in considerable amount.* This substance is acid in character, and gives a deep violet coloration with alcoholic ferric chloride, which at first led to the belief that it was a 1 : 3-diketone, but further investigation showed that the ketone groups were in the 1 : 2-position to one another. Like all 1 : 2-diketones, the substance is quantitatively

oxidised by alkaline hydrogen peroxide, the product being *cyclo*-hexane-1 : 1-diacetic acid. From this follows the constitution of the diketone, which must be *cyclo*hexane*spirocyclo*pentane-3 : 4-dione (V).

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix} \rightarrow CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(V.)

The parent member of this group of diketones, *cyclo*pentane-1 : 2-dione (VI), has already been studied by Dieckmann (*Ber.*, 1902, **35**, *3201*), who showed that it is a tautomeric substance of the keto-enol type and reacts in accordance with the formula (VII)

$$CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix} \rightleftharpoons CH_2<\begin{matrix}CH{=}C\cdot OH\\ CH_2\cdot CO\end{matrix}$$

(VI.) (VII.)

when it is treated with reagents for the hydroxyl group. The *cyclo*hexane compound appears to be analogous in every way, and has been characterised by the formation of derivatives.

The formation of the diketone can only be explained by assuming that the original *cyclo*butane-ester undergoes fission by reduction in the strongly reducing medium in which it is formed, with the production of an aldehyde-ester from which alcohol is immediately eliminated with the formation of a diketone :

$$>C<\begin{matrix}CH_2\text{———}\\ CH(CO_2Et)\end{matrix}>CO \rightarrow >C<\begin{matrix}CH_2\cdot CHO\\ CH_2\cdot CO_2Et\end{matrix} \rightarrow >C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}$$

The process thus somewhat resembles the formation of henzoin from two molecules of benzaldehyde. It is, however, distinctly unusual, and experiments have been undertaken in order to shed further light on the subject. It is hoped that by using other condensing agents such as sodamide or sodium ethoxide, ring closure may he effected in a medium not tending to reducc the cyclic compounds formed.

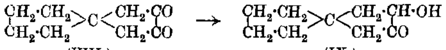
When ββ-dimethylglutaric ester was subjected to the action of sodium or potassium, the course of the reaction was found to be similar, but with important differences. In the first place, no trace of 1 : 1-dimethyl*cyclo*butanone could be detected amongst the neutral products of the reaction, in spite of the most exhaustive search. In the second place, the yield of enolic material was very much smaller, amounting only to some 12—15 per cent. of the theoretical. There can be little doubt that these differences are due to the smaller tendency on the part of ββ-dimethylglutaric ester to pass into the ketonic ester from which the other compounds are

derived, and to the greater instability of the *cyclo*butane ring in this case; this is entirely in accordance with the predictions based on Beesley, Ingold, and Thorpe's hypothesis.

The diketone formed from ββ-dimethylglutaric ester is in every way analogous to the *cyclo*hexane compound described above; it is identical with 1 : 1-dimethyl*cyclo*pentane-3 : 4-dione, which has already been obtained by Thorpe (T., 1911, **99**, 2010) from methyl diketo*apo*camphorate.

It was thought necessary to make certain that the possible formation of 1 : 1-dimethyl*cyclo*butanone was not overlooked on account of its boiling point, which should not be very different from that of xylene, which is used as solvent in this reaction, and would render its separation a matter of difficulty. It was therefore decided to investigate the behaviour of *cyclo*pentanediacetic ester towards potassium.

Now the formation numbers for ketones (or ketonic esters) from this ester and ββ-dimethylglutaric ester are almost identical, but the *spiro*ketone should boil at a considerably higher temperature and should be isolable without difficulty. It is therefore very significant that no trace of such a compound was found in the neutral portion of the reaction mixture. A semicarbazone was isolated from this fraction, but analysis showed that it has the formula $C_{10}H_{17}O_2N_3$, corresponding with a ketone, $C_9H_{14}O_2$ (IX), and this was doubtless derived from the diketone (VIII) by reduction, thus :



(VIII.) (IX.)

*cyclo*Pentane*spirocyclo*pentane-3 : 4-dione (VIII) was isolated from the oil insoluble in sodium hydrogen carbonate solution but soluble in aqueous potassium hydroxide. The yield of this substance was larger than that of the corresponding dimethyl compound, but smaller than that obtained from *cyclo*hexanediacetic ester. The new diketone is in every way analogous to its higher homologue, and has been characterised by the formation of derivatives.

From the above results it is clear that the *cyclo*butane ring is only able to survive the experimental conditions of the Dieckmann reaction when it is combined with a *cyclo*hexane ring, as shown by the fact that *cyclo*hexane*spirocyclo*butanone is the only *cyclo*butane compound isolated in the present investigation; in the other cases the fission of the *cyclo*butane ring with the subsequent formation of a *cyclo*butane ring proceeds to completion. This result is clearly in exact agreement with the theoretical conclusion expressed above.

With regard to the critical formation number, it is felt that definite conclusions cannot be drawn at present. The yields of material traceable to the formation of a *cyclo*butane ring, in the three cases where it has been demonstrated, clearly accord with the predictions based on theoretical figures; but the fact that no such compounds were obtained from glutaric ester is very probably due to another cause altogether. The product, in this case, is obviously of high molecular weight and may be derived from the interaction of two or more molecules of glutaric ester. Such a reaction may depend on the fact that the β-carbon atom is not substituted and can participate in the condensation, whilst this is clearly impossible when the β-carbon atom is quaternary. Further experiments will therefore be necessary to elucidate the point.

EXPERIMENTAL.

The method used in carrying out the experiments with sodium is as follows.

Sodium (9 grams) is melted under dry xylene (50 c.c.) and pulverised by violent shaking. The ester (0·2 gram-mol.) is added to the hot mixture, and the flask, provided with a short air-condenser, is heated in an oil-bath maintained at about 150° for three-quarters of an hour. The sodium gradually dissolves and a brown or red jelly fills the flask. Frequent shaking is necessary to prevent local overheating, leading to decomposition, and it is necessary to add another 25 c.c. of xylene after twenty to thirty minutes to prevent the mass from becoming too solid. When cold, the reaction mixture is decomposed with ice and ice-cold dilute sulphuric acid, which are added with constant shaking; the products of five such operations are combined. The acid aqueous layer is separated from the xylene solution and extracted once with ether, which is then added to the xylene solution. After washing once with water, this solution is thoroughly extracted with aqueous sodium hydrogen carbonate (extract *A*), then twice with ice-cold 15 per cent. aqueous potassium hydroxide (extract *B*).

After washing with water and drying over anhydrous sodium sulphate, the ether–xylene solution can be fractionated with a column; it contains the neutral products of the reaction (mainly unchanged starting-material).

Extract *A* yields on acidification a certain quantity of the original substituted glutaric acid, which can be recovered; it contains practically none of the diketone.

Extract *B*, or "quasi-acid" fraction, is freed from traces of neutral substances by extraction with ether, and acidified with

hydrochloric acid, a rise of temperature being prevented by adding ice to the solution. The precipitated oil, consisting of a diketone and the acid-ester of the corresponding glutaric acid in about equal proportions, is taken up in ether, the solution washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The diketone can then be isolated by distillation under reduced pressure or by conversion into the semicarbazone.

The condensation with potassium is carried out in the same manner, but owing to the very vigorous reaction which takes place it is necessary to allow the "molecular" potassium, to which the requisite additional amount of xylene has been added, to cool completely before the ester is added. The reaction takes place without heating and may become very violent. Vigorous shaking is necessary at this stage, and a fairly long air-condenser should be used to prevent loss. The whole operation occupies a few minutes only. An alternative method consists in gradually adding the ester to the *hot* potassium with constant shaking. The method of working up is the same as with sodium.

There appears to be but little difference in the yields obtained by the two methods, with a slight balance in favour of potassium. The latter is, however, very much more convenient to use, as the long and tedious process of heating the reaction mixture becomes unnecessary.

(I) *Ethyl Glutarate.*

Potassium was used in these experiments. This ester reacts completely, but the product is totally different in character from that produced from the other esters investigated.

In the first place, on adding ice and dilute sulphuric acid to the reaction product it is found that an almost black, gummy material is precipitated, which is almost insoluble both in the aqueous and the xylene–ether layers. It is, however, completely soluble in aqueous sodium hydrogen carbonate, and it is found that, after treatment with the latter, the ethereal solution consists entirely of ether and xylene, and leaves almost no residue on distillation.

The sodium hydrogen carbonate solution, on acidification, yields the gum unchanged, and so far all attempts to isolate a pure substance from this have been fruitless, as it could not be induced to solidify and decomposed when distilled under reduced pressure (12 mm.); it gave an intense colour with alcoholic ferric chloride. An attempt was made to esterify it with alcohol and sulphuric acid in the cold in the hope of obtaining an ester (or ether) which could be distilled. A small amount of distillate was actually obtained, boiling at about 210°/12 mm. and still giving a colour with ferric

chloride, but the analysis gave no clue to its constitution (Found: C = 65·82; H = 8·12 per cent.); the high boiling point indicates beyond doubt that it has a high molecular weight. The substance is probably produced by the interaction of two or more molecules of glutaric ester, and cannot be analogous to the ketonic compounds obtained from other esters of this series.

The presence of *cyclo*butanone in the neutral fraction could not be demonstrated in spite of a careful search.

(II) *Ethyl* cyclo*Hexane-1 : 1-diacetate.*

The yields obtained from 1 gram-mol. of this ester with potassium were usually *cyclo*hexanediacetic acid, and its ester, 35 grams and 50 grams, respectively, and quasi-acid fraction (crude), 70–75 grams.

When the condensations were carried out with sodium, it was found that some of the sodium was left unchanged, and the quantity of sodium had, therefore, to be reduced (from 9 to 7 grams for 0·2 gram-mol.). The yields of quasi-acid fraction were correspondingly small.

Isolation of cyclo*Hexane*spirocyclo*butane-3-one* (I).—This ketone occurs in varying, although always small, amounts in the neutral portion of the reaction product. The fraction boiling between 160° and 250° is treated with semicarbazide acetate in alcoholic solution and allowed to stand. The mixture is diluted with water after twenty-four hours, the dilution usually causing the separation of a certain amount of xylene. As the semicarbazone is appreciably soluble in xylene, light petroleum (b. p. 40—60°) is added at this stage to prevent loss from this cause. The yield of semicarbazone obtained in this way rarely exceeds 1 gram, and in a few experiments much less was obtained. The best yield is about 1 per cent. of the theoretical.

The *semicarbazone* crystallises from dilute alcohol in small needles melting at 204° (Found: C = 61·46; H = 8·82; N = 21·79. $C_{10}H_{17}ON_3$ requires C = 61·51; H = 8·77; N = 21·53 per cent.).

The *ketone* was regenerated from the semicarbazone by boiling with aqueous oxalic acid in a current of steam, and was isolated from the distillate by means of ether. It is a perfectly colourless, mobile liquid, with a characteristic camphoraceous odour, and boils at 208°/751 mm. (thermometer in vapour up to 100°; pure naphthalene boiled at 213·5° under the same conditions) (Found: C = 78·06; H = 10·12. $C_9H_{14}O$ requires C = 78·20; H = 10·21 per cent.).

Soon after distillation the density was found to be 0·96105 at 20·7°. Two days later it was 0·96220, and the refractive indices

determined at the same time were: $n_C = 1{\cdot}46858$; $n_D = 1{\cdot}47113$; $n_F = 1{\cdot}47736$; $n_G = 1{\cdot}48447$. Hence $[R_L]_D = 40{\cdot}14$; $[R_L]_{G-C} = 1{\cdot}156$, and $[R_L]_{F-C} = 0{\cdot}64$, the calculated values being 39·37, 0·99, and 0·60 respectively. All the values thus show considerable exaltation, comparable with those found by Oestling (*loc. cit.*) for nopinone and by Wallach for sabina ketone.

The stability of the ketone towards 1 per cent. aqueous permanganate is considerable, the neutral reagent being scarcely affected for some hours; in the presence of sodium carbonate reduction takes place in about three-quarters of an hour. When boiled in alcoholic solution with *p*-nitrophenylhydrazine, the ketone readily gives a p-*nitrophenylhydrazone*, forming stout, orange needles melting at 137—138° after two crystallisations from dilute alcohol (Found: N = 15·70. $C_{15}H_{19}O_2N_3$ requires N = 15·37 per cent.).

The constitution of the ketone was confirmed by oxidation. When the ketone was dropped into hot dilute nitric acid (*d* 1·2), the action was sluggish, and a little concentrated acid was therefore added. The action then proceeded briskly and was complete in a few minutes. On evaporating the acid liquor, an oily residue was obtained, which soon solidified on scratching and formed feathery aggregates of prisms melting at 132° after two crystallisations from dilute hydrochloric acid. The substance produced in this way was found to be identical with *cyclo*hexane-1-carboxylic-1-acetic acid (II) by direct comparison (mixed melting point) with Norris and Thorpe's specimen * (T., 1921, **119**, 1199) and by analysis (Found: C = 57·84; H = 7·52. Calc., C = 58·04; H = 7·58 per cent.).

Examination of the Quasi-acid Fraction.—The enolic oil obtained from the extract *B* as described on p. 518 boils for the most part between 160° and 175°/20 mm., although a considerable fraction is obtained in the neighbourhood of 200°/20 mm. The lower fraction, on cooling, partly solidifies to a mass of colourless needles, which can be isolated by draining on porous porcelain; the pure substance boils at 158—159°/11 mm.; the yield is 20—25 per cent. of the theoretical.

The substance can be recrystallised from a small amount of light petroleum (b. p. 40—50°); it is extremely soluble in other organic solvents, but almost insoluble in water. The compound separates from a concentrated solution in light petroleum in long needles melting at 67°, but if it is allowed to separate slowly from a more dilute solution, it forms thick, transparent, twinned crystals,

* The melting point of this substance is given (*loc. cit.*) as 134°, but it was found to melt at 132° with the same thermometer and under the same conditions as the above.

belonging to a biaxial system. This compound is cyclo*hexane*-spirocyclo*pentane*-3 : 4-*dione* (V) (Found : C = 72·30 ; H = 8·68. $C_{10}H_{14}O_2$ requires C = 72·25 ; H = 8·49 per cent.).

The diketone gives an intense violet coloration with ferric chloride in alcoholic solution. It is soluble in alkalis, forming a deep red solution, is only partly soluble in alkali carbonates, and does not effervesce with a solution of sodium hydrogen carbonate. With semicarbazide acetate in excess, it forms an extremely insoluble *disemicarbazone*, which melts and decomposes suddenly at 248°. This substance is sufficiently soluble in hot acetic acid to be recrystallised from that solvent, and separates in small, colourless prisms on cooling. It then melts and decomposes at 241° ; the cause of the lowering of the melting point has not been ascertained. For most purposes, the compound is best purified by boiling with alcohol (Found : C = 51·29 ; H = 7·27 ; N = 30·15. $C_{12}H_{20}O_2N_6$ requires C = 51·39 ; H = 7·21 ; N = 29·98 per cent.).

The hydrolysis of this disemicarbazone presents considerable difficulties. Aqueous oxalic acid has but little action owing to the sparing solubility of the compound, whereas mineral acids, especially when moderately concentrated, lead to the formation of a compound, $C_{11}H_{15}ON_3$, which resists further hydrolysis. Five to 10 per cent. aqueous sulphuric acid is the best hydrolytic agent found up to the present and allows a fair yield of the pure diketone to be obtained from the disemicarbazone. The diketone can then be isolated by distillation in a current of steam and extraction of the distillate with ether.

As already mentioned, the use of concentrated mineral acids leads to the production of a compound, $C_{11}H_{15}ON_3$, which is always formed to a certain extent in the hydrolysis of the disemicarbazone and crystallises out on cooling the acid mixture. There is little doubt that this compound is analogous to the triazine obtained by Thiele and Stange (*Annalen*, 1894, **283**, 27) from benzil and semicarbazide, and has the constitution

$$CH_2{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}C{<}{CH_2\cdot C{:}N\cdot C\cdot OH \atop CH_2\cdot C{:}N\cdot N} .$$

It forms buff needles when crystallised from acetic acid, and decomposes at 295° ; it is very sparingly soluble in other organic solvents (Found : C = 64·47 ; H = 7·32 ; N = 20·66. $C_{11}H_{15}ON_3$ requires C = 64·36 ; H = 7·35 ; N = 20·47 per cent.). The compound is soluble in sodium hydroxide solution and dissolves with a deep orange colour in concentrated sulphuric acid.

With *p*-nitrophenylhydrazine the diketone forms a beautifully scarlet *osazone*, which decomposes at 275° and is very sparingly

soluble in most organic solvents. It gives an intense crimson coloration with concentrated sulphuric acid (Found: C = 60·63; H = 5·76. $C_{22}H_{24}O_4N_6$ requires C = 60·51; H = 5·55 per cent.).

o-Phenylenediamine readily condenses when warmed with the diketone in alcoholic solution for a few minutes. The *quinoxaline* derivative, $C_5H_{10}{>}C{<}{\genfrac{}{}{0pt}{}{CH_2{\cdot}C{:}N}{CH_2{\cdot}C{:}N}}{>}C_6H_4$, crystallises from dilute alcohol in beautiful, silky, flattened needles melting at 99—100° and retaining a buff tint even on repeated crystallisation (Found: C = 80·46; H = 7·77. $C_{16}H_{18}N_2$ requires C = 80·63; N = 7·60 per cent.).

An *anil*, $C_5H_{10}{>}C{<}{\genfrac{}{}{0pt}{}{CH{=}C{\cdot}OH}{CH_2{\cdot}C{:}NPh}}$, is also readily obtained and melts at 106°; it forms lustrous, colourless, needles from dilute alcohol (Found: C = 79·20; H = 8·08. $C_{16}H_{19}ON$ requires C = 79·60; H = 7·96 per cent.).

The *benzoyl* derivative, $C_5H_{10}{>}C{<}{\genfrac{}{}{0pt}{}{CH{=}C{\cdot}O{\cdot}COPh}{CH_2{\cdot}CO}}$, was prepared by warming the diketone in ethereal solution with benzoyl chloride and pyridine. It crystallises from light petroleum (b. p. 40—50°) in spherical clusters of colourless needles melting at 69—70° (Found: C = 75·46; H = 6·97. $C_{17}H_{18}O_3$ requires C = 75·51; H = 6·70 per cent.).

The constitution of the diketone was finally confirmed by oxidation. The diketone (0·5 gram) was dissolved in 10 c.c. of 10 per cent. aqueous sodium carbonate, and 25 c.c. of 6 per cent. hydrogen peroxide were added. A brisk evolution of gas soon occurred and the liquid became warm. It was acidified after about two hours, when a crystalline acid was precipitated; a further crop was obtained by extracting the mother-liquors with ether. The acid was identified as *cyclo*hexane-1 : 1-diacetic acid by direct comparison (mixed melting point) and by analysis (Found: C = 60·08; H = 8·08. Calc., C = 59·98; H = 8·05 per cent.).

In addition to the diketone melting at 67° there is another enolic substance which is present in small quantity in the original extract *B*. It is found in the fraction of higher boiling point (about 180°/20 mm.) and partly separates in the solid state. The solid can be crystallised from a mixture of ether and light petroleum (b. p. 40—50°) and is obtained in small, colourless plates melting at 135—136°. It develops an intense violet coloration with alcoholic ferric chloride; its composition corresponds with the formula $C_{12}H_{18}O_2$ (Found: C = 73·92; H = 9·33. Calc., C = 74·20; H = 9·33 per cent.), but the constitution of the substance has not yet been elucidated.

The less volatile oil obtained from the quasi-acid fraction consists of the acid-ester of *cyclo*hexanediacetic acid, although a little of the diketone is still present, as shown by the somewhat high percentage of carbon found on analysis (Found: C = 64·13; H = 8·76. $C_{12}H_{20}O_4$ requires C = 63·12; H = 8·85 per cent.). It yields *cyclo*hexanediacetic acid on hydrolysis.

(III) *Ethyl ββ-Dimethylglutarate.*

Potassium was almost exclusively used as a condensing agent. The yields were ββ-dimethylglutaric acid * and its ester, 30 grams and 52 grams respectively, and quasi-acid fraction, 16 grams. In spite of the most searching investigation, the formation of 1 : 1-dimethyl*cyclo*butane-2-one could not be demonstrated.

Examination of the Quasi-acid Fraction.—As far as could be ascertained, only one substance occurs in this fraction; it is best separated in the form of its sparingly soluble *disemicarbazone*, which is readily formed under the ordinary conditions. It is a microcrystalline powder decomposing at 257° with previous darkening; crystallisation from acetic acid lowers the decomposition point to 251° (compare p. 522) (Found: C = 45·04; H = 6·80. $C_9H_{16}O_2N_6$ requires C = 44·98; N = 6·71 per cent.).

This disemicarbazone is more readily hydrolysed than the corresponding *cyclo*hexane compound, and a 60 per cent. yield of pure 1 : 1-dimethyl*cyclo*pentane-3 : 4-dione is easily obtained from it by means of an excess of 10 per cent. aqueous sulphuric acid. The yield of diketone appears to be barely 8 per cent. of the theoretical. The diketone is isolated by distillation in a current of steam and can be extracted from the distillate, previously saturated with ammonium sulphate, by means of ether. On removing the solvent, the diketone usually remains in the superfused state, but it can be made to crystallise immediately on introducing a crystal of the solid. It crystallises beautifully from light petroleum (b. p. 40—50°) in large plates resembling mica and melting at 45°, identical with the substance obtained by Thorpe (*loc. cit.*) from methyl diketo*apo*camphorate by hydrolysis (mixed melting point) (Found: C = 66·32; H = 7·97. Calc., C = 66·61; H = 7·93 per cent.). The diketone gives a deep purplish-red colour with ferric chloride and is appreciably soluble in water.

The *quinoxaline* derivative, $Me_2C\left<\begin{matrix}CH_2\cdot C:N\\ CH_2\cdot C:N\end{matrix}\right>C_6H_4$, is readily formed by warming 0·3 gram of the diketone in alcoholic solution with an equal weight of *o*-phenylenediamine for a few minutes,

* Some of the acid is lost owing to its great solubility in water.

the alcohol being allowed to evaporate off on the steam-bath. On scratching, the mass solidifies. The product, crystallised from dilute alcohol, forms magnificent, flattened needles, m. p. 123·5° (*Found*: C = 78·81; H = 7·14. $C_{13}H_{14}N_2$ *requires* C = 78·73; H = 7·12 per cent.).

The coustitution of the diketone was confirmed by oxidation as in the case of the *cyclo*hexane compound. The acid, obtained in quantitative yield by the action of hydrogen peroxide in alkaline solution, melted at 101° and was proved to be ββ-dimethylglutaric acid by direct comparison (mixed melting point) with a genuine specimen and by analysis (Found: C = 52·49; H = 7·52. Calc., C = 52·47; H = 7·56 per cent.).

(IV) *Ethyl* cyclo*Pentanediacetate.*

This ester, prepared by esterifying the acid with alcohol and sulphuric acid, *is a colourless liquid boiling at* 157—158°/16 *mm.* (Found: C = 64·29; H = 9·09. $C_{13}H_{22}O_4$ requires C = 64·13; H = 9·13 per cent.).

The yields obtained from 1 gram-mol. of the ester, by interaction with potassium, were *cyclo*pentanediacetic acid and its ester, 30 grams and 55 grams respectively, and the quasi-acid fraction (crude), 54 grams.

The neutral fraction was carefully searched for the presence of a ketone, $C_8H_{12}O$, but this has not, up to the present, been detected: it was invariably found, however, that the acid *diketone* was not completely extracted by treatment with potassium hydroxide, and the neutral fraction still gave a faint coloration with ferric chloride. On prolonged standing with alcoholic semicarbazide acetate, a little of the disemicarbazone (decomp. 252°; see p. 526) was obtained. In addition to this, a semicarbazone soluble in alcohol was also produced. It was purified by crystallisation from dilute alcohol and formed stout, transparent crystals decomposing without darkening at 183—184° (Found: C = 56·43; H = 8·20; N = 20·22. $C_{10}H_{17}O_2N_3$ requires C = 56·85; H = 8·10; N = 19·94 per cent.). It appears probable that the corresponding ketone has the constitution IX.

Examination of the Quasi-acid Fraction.—This fraction consists of equal quantities of the acid ester * and the diketone VIII, which boils for the most part at 148°/13 mm. and immediately solidifies on cooling; the yield is about 18 per cent. of the theoretical. It can be purified by crystallisation from light petroleum (b. p. 40—50°), in which it is somewhat sparingly soluble. From this

* This was confirmed by hydrolysis to *cyclo*pentanediacetic acid.

solvent it separates in fine, sparkling plates melting at 110—111°. The compound is cyclo*pentane*spirocyclo*pentane*-3 : 4-*dione* (Found : C = 71·03; H = 7·81. $C_9H_{12}O_2$ requires C = 71·00; H = 7·96 per cent.). In alcoholic solution it gives an intense dark red colour with ferric chloride.

The *disemicarbazone* is a microcrystalline powder almost insoluble in alcohol, and decomposes at 252° (Found : C = 49·16; H = 6·96. $C_{11}H_{18}O_2N_6$ requires C = 49·60; H = 6·80 per cent.)

The *quinoxaline* derivative, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot C{:}N\\ CH_2\cdot C{:}N\end{matrix}\!>\!C_6H_4$, is readily formed by the usual method, but is somewhat difficult to purify. It separates from dilute alcohol in buff needles and melts at 95—96° (Found: C = 79·84; H = 7·19. $C_{15}H_{16}N_2$ requires C = 80·32; H = 7·19 per cent.).

In conclusion, the author's best thanks are due to Professor J. F. Thorpe, F.R.S., for his kind interest in the progress of the investigation.

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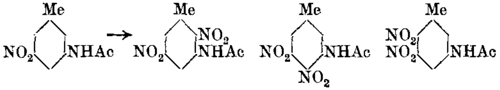
LXI.—*The Dinitrotoluidines.*

By OSCAR LISLE BRADY, JAMES NELSON EDMUND DAY, and WILLIAM JOSEPH WOODGATE ROLT.

DURING the course of earlier investigations on the synthesis of 2 : 3 : 6-trinitrotoluene (Brady and Taylor, T., 1920, **117**, 876) and of 3 : 4-dinitrotoluene (Brady and Williams, *ibid.*, p. 1137), a marked difference was observed in the behaviour of some of the dinitrotoluidines on diazotisation and on oxidation with monopersulphuric acid, depending, apparently, on the relative positions of the groups. This seemed to offer an opportunity for the study of the effect of the position and number of other substituents on the reactivity, apart from mobility, of the amino-group in the benzene ring. The present paper is an account of preliminary preparative work. Sixteen dinitrotoluidines should exist; of these, eleven have been described, and two others have been prepared by other workers, although their results have not yet been published. Three, therefore, remained, namely, 2 : 5-dinitro-*m*-toluidine, 4 : 5-dinitro-*m*-toluidine, and 5 : 6-dinitro-*m*-toluidine. An attempt has been made to prepare these three

compounds in order that a complete series should be available for further investigation; a certain amount of interest also was attached to the fact that in no case had as many as sixteen position-isomerides been obtained in benzenoid compounds. It might be expected that the nitration of 5-nitroaceto-*m*-toluidide would give a mixture of the acetyl derivatives of the required compounds from which the amines could be obtained by hydrolysis.



It has been found, however, that only the last two compounds are formed or if any 2 : 5-dinitroaceto-*m*-toluidide is produced it is only in very small quantities. It is remarkable that the presence or absence of sulphuric acid in the nitration has very great influence on the position taken up by the entering nitro-group. If a solution of 5-nitroaceto-*m*-toluidide in concentrated sulphuric acid is added to nitric acid or if the solid acetyl compound is added to a mixture of nitric and sulphuric acids, 5 : 6-dinitroaceto-*m*-toluidide will form the bulk of the product, but if the acetyl compound is added directly to fuming nitric acid, 4 : 5-dinitroaceto-*m*-toluidide will preponderate. The mixtures have been separated by fractional crystallisation of the acetyl derivatives and of the amines from various solvents, and careful search has been made for the third isomeride. The compounds obtained have been oriented by conversion into the corresponding dinitrotoluenes through the diazo-reaction. The method of preparation of the starting-material, 5-nitroaceto-*m*-toluidide, may be summarised: aceto-*p*-toluidide ⟶ 3 : 5-dinitroaceto-*p*-toluidide ⟶ 3 : 5-dinitro-*p*-toluidine ⟶ 3 : 5-dinitrotoluene ⟶ 5-nitro-*m*-toluidine ⟶ 5-nitroaceto-*m*-toluidide. These operations were somewhat laborious, and a considerable amount of study has been given to the various stages and certain improvements of method introduced.

EXPERIMENTAL.

5-Nitro-m-*toluidine*.—The starting-material for the preparation of this compound was aceto-*p*-toluidide, from which 3 : 5-dinitro-*p*-toluidine was obtained by a modification of the methods of Beilstein and Kuhlberg (*Annalen*, 1871, **158**, 341) and Jackson and Ittner (*Amer. Chem. J.*, 1897, **19**, 6). It is inadvisable to nitrate large quantities at a time, as tarry products are then formed in the subsequent hydrolysis owing to difficulty in washing a large

amount of precipitate; so 20-gram quantities were employed. Twenty grams of aceto-*p*-toluidide were added in small portions at a time during thirty minutes to 200 c.c. of commercial fuming nitric acid kept below 15°. Jackson and Ittner used a smaller amount of acid distilled from equimolecular quantities of potassium nitrate and concentrated sulphuric acid, but a special acid is not necessary. The solid dissolved at once with considerable evolution of heat. When all had been added, the solution was poured into a large amount of well-stirred ice water, and the precipitated 3 : 5-dinitroaceto-*p*-toluidide filtered off at once and thoroughly washed with water. Rapid filtration and thorough washing were imperative, as the dinitroacetotoluidide was very readily hydrolysed by the dilute nitric acid and the amine formed was acted on by the nitrous acid also present, with the production of tarry products. The use of a larger quantity of nitric acid than that given resulted in a great diminution of yield. The washed precipitate was freed from water as much as possible by the aid of the pump and hydrolysed by heating with a mixture of 50 c.c. of concentrated sulphuric acid and 50 c.c. of water for an hour on the water-bath. The pale yellow acetyl compound suspended in the liquid was replaced by the deep yellow amine, which, after cooling, was filtered through glass wool, washed with a small quantity of 50 per cent. sulphuric acid, then with water, and dried. This method of hydrolysis is preferable to that of Jackson and Ittner, who use a more dilute acid at its boiling point and dilute somewhat before filtering; any mono-nitrotoluidine present is soluble in the stronger acid, but there is some danger of its being precipitated if a more dilute one is used. Beilstein and Kuhlberg's method with alcoholic potassium hydroxide never gives so clean a product nor so good a yield. The 3 : 5-dinitro-*p*-toluidine obtained was almost pure and melted at 165—168°; the yield was 54 per cent. of the calculated quantity. Attempts to improve the yield by nitrating in acetic acid solution were not successful, as oily products were obtained.

3 : 5-Dinitrotoluene was prepared from 3 : 5-dinitro-*p*-toluidine by diazotising in boiling alcoholic solution by the method of Cohen and McCandlish (T., 1905, **87**, 1270). The yield was only 80 per cent. of that calculated, although Cohen and McCandlish claim that they obtained almost quantitative results. Wheeler (*Amer. Chem. J.*, 1910, **44**, 144), however, using a similar method, claims but a 70 per cent. yield. 3 : 5-Dinitrotoluene is best purified from the traces of tarry material formed during the diazotisation by heating on the water-bath for thirty minutes with 70 per cent. nitric acid, pouring into water, drying the precipitate, and crystallising from benzene and light petroleum.

The reduction of 3 : 5-dinitrotoluene to 5-nitro-*m*-toluidine has been described by Nevile and Winther (*Ber.*, 1882, **15**, 2985), but they did not obtain very good results. The following method gave an 80 per cent. yield of an almost pure compound. Ten grams of 3 : 5-dinitrotoluene were dissolved in 100 c.c. of alcohol, and 60 c.c. of ammonium sulphide (15 per cent.) added. The mixture was boiled for an hour under reflux, the hot solution filtered, diluted with a large volume of water, and the precipitate obtained was extracted with boiling hydrochloric acid repeatedly until the extract no longer gave a precipitate with ammonia. The extracts were cooled, and the 5-nitro-*m*-toluidine precipitated by the addition of ammonia.

Under careful working conditions there should be no great difficulty in obtaining a 30 per cent. yield of this compound calculated on the aceto-*p*-toluidide employed, although a large number of operations are necessary to obtain any quantity of material, as working with large amounts does not result in proportionate yields and the products are often far less pure. As we had to gain experience, our total yield over a large number of experiments was 20 per cent.

*5-Nitroaceto-*m*-toluidide.*—Five grams of 5-nitro-*m*-toluidine were added to 30 grams of cold acetic anhydride, when a vigorous reaction took place and the mixture became almost solid. The mixture was warmed until complete solution occurred, and was then left to cool slowly. The *5-nitroaceto-m-toluidide* crystallised out, very little remaining in solution. After filtering and drying, it could be crystallised from benzene, from which it separated as a white, microcrystalline powder melting at 187° (Found : N = 14·2. $C_9H_{10}O_3N_2$ requires N = 14·4 per cent.). The crude compound was almost pure and was used without recrystallisation.

*Nitration of 5-Nitroaceto-*m*-toluidide.*—Three methods of nitration were investigated, as conditions of nitration frequently alter the relative amounts of the isomerides formed. Not more than 5 grams of material were nitrated at one time, several nitrations being done in each case and the products worked up together.

(1) Five grams of 5-nitroaceto-*m*-toluidide were dissolved in small portions at a time in 25 c.c. of concentrated sulphuric acid, cooled in ice, and the solution was added during forty minutes to 18 c.c. of nitric acid (*d* 1·5), the mixture being kept below 9°. The mixture was left on ice for a further forty minutes, poured on to crushed ice, and the precipitated mixture of dinitroacetotoluidides filtered and washed thoroughly with water. The moist product was crystallised from dilute alcohol and, after drying, from acetic anhydride. In this way a compound was obtained melting at

172°; further crystallisation did not raise this melting point. This compound was found to be 5 : 6-dinitroaceto-*m*-toluidide and formed the greater part of the product of reaction. The filtrates from the crystallisations from alcohol and acetic anhydride were diluted with water, and the precipitate obtained was hydrolysed with 50 per cent. (by weight) sulphuric acid on the water-bath. Almost all passed into solution, the small residue which was filtered off from the hot solution yielding only a little 5 : 6-dinitroaceto-*m*-toluidide. The solution was diluted with water and filtered. The filtrate yielded, on neutralising with ammonia and leaving for several days, a precipitate too small for further examination. The solid was crystallised from alcohol, when a material melting at 150—162° was obtained, which, on crystallisation from benzene, gave a compound melting at 162—163°; this proved to be slightly impure 5 : 6-dinitro-*m*-toluidine. The alcoholic mother-liquors, on dilution, gave a product melting at 100—120°, which, on crystallisation from benzene, gave a less pure 5 : 6-dinitro-*m*-toluidine. The benzene mother-liquors from the above crystallisations were evaporated, and the residue was crystallised from glacial acetic acid, when what appeared to be 4 : 5-dinitro-*m*-toluidine was deposited, but the substance was obtained in so small amount as to render its identification not quite certain.

The filtrate from the diluted nitration mixture was neutralised with ammonia and left for several days. A small quantity of solid separated, which was crystallised from acetic anhydride and found to be 4 : 5-dinitroaceto-*m*-toluidide. The mother-liquors from this crystallisation, on dilution and crystallisation of the precipitate from alcohol, yielded a further quantity of this compound.

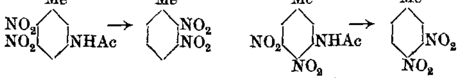
In none of the fractionations was any indication obtained of the presence of the 2 : 5-dinitro-substituted compounds.

(2) Five grams of 5-nitroaceto-*m*-toluidide were added, in small portions at a time, during fifteen minutes to 50 c.c. of nitric acid (*d* 1·5) kept at 2—3°. The mixture was left for forty-five minutes on ice, then poured on to crushed ice, and the precipitate filtered and thoroughly washed with water. The solid was crystallised from alcohol, when a product was obtained melting, alone, at 175°, mixed with 5 : 6-dinitroaceto-*m*-toluidide (m. p. 172°), at 150°, and with 5-nitroaceto-*m*-toluidide (m. p. 187°), at 165°. A second crystallisation from alcohol gave a pure compound melting at 177°, which was found to be 4 : 5-dinitroaceto-*m*-toluidide. The mother-liquors from the alcohol crystallisations were diluted, and the precipitate was hydrolysed with 50 per cent. sulphuric acid on the water-bath for one and a half hours. Almost complete solution took place, the residue being too small for further investigation.

The mixture was diluted, filtered, and the solid dried and crystallised from benzene, when a fair amount of 5 : 6-dinitro-*m*-toluidine was obtained. The benzene mother-liquors were investigated for the presence of 2 : 5-dinitro-*m*-toluidine, but no evidence of its presence was obtained. The filtrate from the diluted nitration mixture yielded but a small amount of solid on neutralisation, which was not investigated.

(3) The first nitrations were carried out by adding gradually 5 grams of finely powdered 5-nitroaceto-*m*-toluidide to a mixture of 20 c.c. of nitric acid (*d* 1·5) and 32 c.c. of concentrated sulphuric acid cooled in ice. The solid dissolved slowly, and after thirty minutes the solution was poured on to crushed ice, and the precipitate filtered, thoroughly washed, and crystallised, first from alcohol and then, after drying, from acetic anhydride, when 5 : 6-dinitroaceto-*m*-toluidide was obtained. The mother-liquors were diluted, and the precipitate obtained was hydrolysed and examined on much the same lines as have been described above. This method was employed only in preliminary experiments to determine the best methods of crystallising and separating the various compounds. It was abandoned in favour of the somewhat cleaner method described in (1), as difficulties arose in adding a solid to the mixed acids which dissolved it but slowly. It is only necessary to state, therefore, that only 5 : 6-dinitro-derivatives were isolated from the products and no evidence of the presence of 2 : 5-dinitro-compounds was obtained.

Orientation.—The two acetotoluidides were oriented by dissolving 0·5 gram of the material in a mixture of 20 c.c. of absolute alcohol and 5 c.c. of fuming sulphuric acid (20 per cent. of SO_3), heating for a short time on the water-bath to ensure hydrolysis, and then adding 3 grams of dry, powdered sodium nitrite in small portions at a time. When the action had moderated, the mixture was heated on the water-bath for a few minutes, diluted with water, and distilled in steam. The dinitrotoluene was extracted from the distillate with ether, the ether evaporated, and the residue crystallised from dilute alcohol and identified by its melting point and by the melting points of its mixtures with the various dinitrotoluenes. The compound melting at 172° gave 2 : 3-dinitrotoluene, and that melting at 177° gave 3 : 4-dinitrotoluene.



M. p. 172°. M. p. 177°.

*Hydrolysis of the Dinitroaceto-*m*-toluidides.*—5 : 6-Dinitroaceto-*m*-toluidide was hydrolysed by heating on the water-bath with 50 per cent. sulphuric acid for an hour. A clear solution was obtained, and on dilution the amine was precipitated as a yellow crystalline product, which was crystallised from alcohol. 4 : 5-Dinitroaceto-*m*-toluidide, when treated in a similar manner, was but slowly attacked, so alcohol was added until a clear solution was obtained, the mixture heated on the water-bath for forty-five minutes, diluted, and the precipitated amine crystallised from alcohol.

5 : 6-*Dinitroaceto-*m*-toluidide* crystallises from acetic anhydride as a faintly yellow, sandy powder melting at 172° (Found : N = 17·9. $C_9H_9O_5N_3$ requires N = 17·6 per cent.).

4 : 5-*Dinitroaceto-*m*-toluidide* crystallises from alcohol in fine, white needles melting at 177° (Found: N = 17·6. $C_9H_9O_5N_3$ requires N = 17·6 per cent.).

5 : 6-*Dinitro-*m*-toluidine* crystallises from benzene in orange-yellow plates melting at 165° (Found: N = 21·6. $C_7H_7O_4N_3$ requires N = 21·3 per cent.). This compound gave 2 : 3-dinitrotoluene when the amino-group was removed by diazotising and boiling with alcohol as above.

4 : 5-*Dinitro-*m*-toluidine* crystallises from alcohol in large, brownish-yellow needles melting at 141° (Found: N = 21·5. $C_7H_7O_4N_3$ requires N = 21·3 per cent.). On removal of the amino-group, it gave 3 : 4-dinitrotoluene.

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University College, London. [*Received, March 1st, 1922.*]

LXII.—*The Rotatory Dispersive Power of Organic Compounds. Part X. The Preparation and Properties of Pure Ethyl Tartrate.*

By Thomas Martin Lowry and John Outram Cutter.

In a series of experiments to determine the form of the curves of rotatory dispersion of the tartaric esters (Lowry and Dickson, T., 1915, **107**, 1176; Lowry and Abram, *ibid.*, p. 1187), difficulty was experienced in obtaining accurate data for ethyl tartrate, since it was found that the samples used not only varied in rotatory power, but could also be separated by distillation into fractions of

unequal optical activity, the middle fractions giving higher readings than the two end fractions. In the case of methyl tartrate, this difficulty was not experienced, and the methyl ester was therefore selected as affording the most trustworthy material for determining the mathematical equation for the dispersion curves. No further attempt was made at that time to isolate pure ethyl tartrate, but it was suggested (*loc. cit.*, p. 1177) that, in view of the large amount of work that had been done with this ester, it was very desirable that a complete fractionation should be carried out sooner or later, in order that the properties of the compound might be determined with the help of fully purified material.

In response to this suggestion, Professor Franchimont of Leiden wrote to say that more than twenty years previously the ester had been prepared in his laboratory as a crystalline solid, which, after purification with the help of a centrifugal machine, melted at 16—17°, and remained for many years in the solid state when stored in a cellar below this temperature. The crystalline ester had been prepared again in his laboratory in 1907, and on this occasion the melting point had been raised to 19°. Since it was evident that material which had been purified by crystallisation was likely to be better than any that could be obtained by fractional distillation only, Professor Franchimont very kindly prepared and sent to London two fresh specimens of the crystallino ester. The first specimen melted at 6° and about half of it remained liquid at 0°. The low melting point showed that it was not completely purified, but its rotatory power, $\alpha_{5461} = +55{\cdot}86°$, $\alpha_{4358} = +13{\cdot}06°$, measured in a 6-decimetre tube at 20°, was already almost equal to the highest value that had been obtained with material purified by fractional distillation. The second specimen had been fully purified in Holland, although its melting point had not been determined. As it had become liquid in transit, and the package had been opened by the Customs officers, the specimen was refrozen in London, when it was found that it began to melt at 19°, whilst its rotatory power was $\alpha_{5461} = +56{\cdot}48°$, $\alpha_{4358} = +14{\cdot}34°$.

After the samples of ethyl tartrate which had been purified in Holland had been persuaded to crystallise in London (by freezing to a glass with solid carbon dioxide and then thawing in an ice-chest), no difficulty was experienced in inoculating other specimens of the tartrate with the crystals, and obtaining in this way several kilograms of the solid ester. This was purified by draining in a centrifugal machine and freed from the last traces of water by distillation under very low pressure. The purification was continued until both the rotatory power and the melting point were constant. Thus, fractions prepared by different methods and puri-

fied independently melted concordantly at 18·7° and gave an observed rotation $\alpha_{5461} = + 56·9°$ for a 6-decimetre column at 20°.

With the help of this pure material the most important of the physical constants of the ester were determined, including the density at three temperatures, the viscosity, the refractive index for eight wave-lengths in the visible spectrum, and finally the optical rotatory power for a long series of lines in the visible and early ultra-violet regions of the spectrum. The last series of readings was of special significance, as showing that pure ethyl tartrate gives, like the methyl ester, a curve of rotatory dispersion which can be expressed right up to the limits of experimental accuracy by two terms of the Drude equation. In the case of the acid, the dispersion is apparently rendered more complex as a result of electrolytic dissociation, since small but systematic differences are found between the observed rotations of the acid, in aqueous solutions of different concentrations, and the values calculated from the two-term equation (Lowry and Austin, Bakerian Lecture, *Phil. Trans.*, 1922). In the case of the ethyl ester, however, the largest deviation between the observed and calculated values for the specific rotatory power is only 0·03° (for a very difficult zinc blue line) in a series of eighteen visual readings and 0·3° for the worst of the photographic readings in the ultra-violet region of the spectrum; for two-thirds of the readings the differences are ± and the remaining errors are distributed casually. It is therefore clear that the two-term formula expresses perfectly the rotatory dispersion of the ester, as at present determined, and will probably remain as an exact representation of that dispersion until entirely new methods of measurement shall be developed.

EXPERIMENTAL.

Preparation of Ethyl Tartrate.

(*a*) The material used for these experiments was at first prepared as described by Patterson (T., 1910, **79**, 168), using hydrogen chloride as a condensing agent; but the yields obtained were low (56 per cent.), and even after two distillations under a pressure of 10 to 12 mm. the product still contained chlorine.

(*b*) Much better results were obtained by using a modified form of the method described by Rodger and Brame (T., 1898, **73**, 302), in which the acid is first converted into ethyl hydrogen tartrate by boiling with alcohol and distilling off the aqueous liquor, and then into the normal tartrate by boiling with more alcohol and fractionating out the ester under reduced pressure. In practice, 1,200 grams of tartaric acid were boiled for seven hours with 2,000

grams of freshly distilled 98 per cent. alcohol in a 5-litre flask heated in an oil-bath at 115°; the aqueous liquor was then distilled off rapidly by raising the temperature of the oil-bath to 250°. The syrupy residue was heated with 400 grams of fresh alcohol during a further period of seven hours, the temperature of the oil-bath being 150—160°, after which the aqueous liquor was again distilled off as before. The crude ester was distilled, in quantities of 150 to 200 grams at a time, in a 1½-litre distilling flask under a pressure of 10 to 12 mm.; when the pressure rose to 15 mm., distillation was stopped. In this way an immediate yield of 700 to 800 grams of a water-white ester was obtained from 1,200 grams of acid. The residues from the vacuum distillation were boiled with a further quantity of alcohol for another period of seven hours, and distilled as described above to obtain a further quantity of the ester; but this process could not be repeated more than three times owing to excessive frothing in the final distillation. Altogether, 7,800 grams of the ester were prepared by this method, with a yield of about 80 per cent.

(c) A small quantity of the ester was also prepared by heating the crude ethyl hydrogen tartrate [prepared as described under (b) above] with four times its weight of 98 per cent. alcohol during a period of five hours at 160° in a rotating autoclave (Morgan and Vining, T., 1920, **117**, 780) at a pressure of 200 lb. per square inch. The subsequent distillation was carried out as before, but there was no frothing, and an immediate yield of more than 90 per cent. of very pure material was obtained. This method has also been applied with great advantage in the preparation of propyl tartrate.

Purification.

The ester, prepared as described above, was cooled in ice, inoculated with a crystal of ethyl tartrate, and frozen to a solid block. The mass was broken up and the lumps were crushed, in which process they were partly melted, giving rise to a sludge of crystals in a very syrupy liquid. This was transferred to a small centrifuge, the cage of which had been lined with silk. After draining, the crystals were again partly melted and centrifuged, whilst the mother-liquors were frozen to produce a further crop of crystals.

Ethyl tartrate appears to be almost as hygroscopic as sulphuric acid; the crystals therefore always absorb moisture during the process of freezing and draining. This is not altogether a disadvantage, since it provides a liquor of lower melting point which may very well serve as a rinsing agent to remove the impurities;

but in order to obtain the pure ester, the crystals must be melted and distilled to get rid of the last traces of water. This distillation was at first carried out under a pressure of 11 to 12 mm. with the help of two water-pumps arranged in parallel. In the later stages of the work a Langmuir mercury-vapour pump was used, in conjunction with an oil-pump of the Siemens type, the oil-pump being backed by two water-pumps in parallel. The capacity of this combination is enormous, since that of the mercury-pump is said to be fifteen times as great as that of the oil-pump, which is itself very large. In practice, the distillation of the ester could be carried out under pressures of 0·03—0·001 mm. as recorded by a McLeod gauge. In contrast to the high capacity of this combination, it may be stated that a Gaede mercury-pump of the ordinary type gave results which were no better than those obtained by means of a water-pump alone, since the pressure always rose to several millimetres of mercury as soon as distillation began.

In order to secure useful results in this system of low-pressure distillation, the whole of the distillation apparatus was made of glass, with ground joints lubricated and sealed with ethyl tartrate and all the connexions were at least 1 centimetre, and usually 2 centimetres, in diameter. A drying tube of large diameter containing phosphoric oxide was inserted between the distillation apparatus and the Langmuir pump in order to keep out all traces of moisture. The liquid was heated in an oil-bath, and evaporated quietly without any bumping or even formation of bubbles; indeed, the only indication that distillation was proceeding was the gradual accumulation of liquid in the iced receiver. In this apparatus the temperature of distillation was brought down from 160—170° to 98—110°, although by rapid heating the temperature could be raised to 115°.

Fractionation.

The two samples used were:

(i) 4,000 grams; $\alpha_{5461} = 53·62°$ (6 dcm.). Freezing point 7°.
(ii) 3,800 grams; $\alpha_{5461} = 54·68°$. Freezing point 7°.

After freezing, partial melting, and centrifuging, the values of the constants were:

(i) $\alpha_{5461} = 55·06°$. Freezing point 14·5°.
(ii) $\alpha_{5461} = 55·02°$. Freezing point 13·4°.

Three further freezings, after mixing these two fractions, and one distillation under 10 mm. pressure, gave the values:

$\alpha_{5461} = 56·62°$. Freezing point 18·7°;

and similar treatment of all the mother-liquors obtained up to this point gave :

$$\alpha_{5461} = 56{\cdot}60^\circ. \quad \text{Freezing point } 17{\cdot}8^\circ.$$

These two fractions, when mixed and fractionally crystallised, gave :

Solid	$\alpha_{5461} = 56{\cdot}62^\circ$.	Freezing point 17·8°.
Liquid	$\alpha_{5461} = 56{\cdot}60^\circ$.	Freezing point 17·8°,

but when redistilled a fortnight later the rotatory power was found to have fallen from 56·6° to 56·2°. We believe that this drop of rotatory power is the direct result of distilling the ester in a relatively poor vacuum, and all the rotatory powers given above may be too low from this cause, since every fraction was distilled before its rotatory power was determined. By using the Langmuir pump for the final distillation, higher rotatory powers were obtained, although the quantity of material only allowed 2-decimetre tubes to be used, for example, the sample described above gave the following fractions :

Fraction	1*	$\alpha_{5461} = 18{\cdot}8^\circ$ (2 dcm.).	Freezing point 18·4°.
,,	2*a*	,, $= 19{\cdot}01^\circ$.	,, ,, 18·7°.
,,	2*b*	,, $= 19{\cdot}02^\circ$.	,, ,, 18·7°.
,,	3	,, $= 18{\cdot}99^\circ$.	,, ,, 18·7°.

* Probably moist.

The 500 grams prepared in an autoclave gave on distillation a large middle fraction of 450 grams, and on redistillation another middle fraction of 400 grams; the values for the latter were :

$$\alpha_{5461} = 19{\cdot}01^\circ. \quad \text{Freezing point } 18{\cdot}7^\circ.$$

It appears, therefore, that preparation in an autoclave followed by two distillations under a pressure of less than 0·1 mm. provides an alternative method of preparing the ester in a pure condition.

Coloration.

Almost all commercial samples of ethyl tartrate are yellow in colour, perhaps as a result of careless distillation. A similar colour was also seen in one of our own samples. This colour is undoubtedly due to an impurity, since it can be removed by freezing out and centrifuging the crystalline ester. When this permanent coloration had been removed, it did not reappear in six successive distillations under 10 mm. pressure; but after the rotatory power had risen to 56·28°, the purified ester developed a yellow colour when heated in the distilling flask, and gave a yellow distillate, the colour of which disappeared, however, after a few hours. This

transient yellow colour reappeared in every subsequent distillation and became very pronounced when the rotatory power had risen to 56·62°.

The yellow colour, which thus appears when highly purified samples are distilled, does not produce any substantial alteration of rotatory power. Thus when two separate samples were distilled and their rotations taken, first whilst still coloured, and secondly after becoming colourless, the readings in 2-decimetre tubes were

Sample 1. Coloured, 18·90°. Colourless, 18·85°.
Sample 2. Coloured, 18·88°. Colourless, 18·85°.

In the same way, of two samples which (as set out in a previous paragraph) gave rotations of 56·62° and 56·60° in 6-decimetre tubes one was quite light in tint, whilst the other developed an intense yellow in the last distillation.

Slow or rapid distillation, and the presence of rubber stoppers in the apparatus, were suspected as causes producing the transient yellow coloration, but without justification. Thus, the sample of ethyl tartrate which was prepared in an autoclave never came into contact with rubber; it was distilled once in the vacuum of the Langmuir pump, in an apparatus composed entirely of glass, and gave a perfectly colourless distillate; but when the pure middle fraction was again distilled under the same conditions, it developed the familiar transient yellow colour. This colour must, indeed, be regarded as a test which serves to establish the *purity* rather than the *impurity* of the sample.

The failure of the yellow colour to appear in the early stages of purification might have been attributed to the presence in the distillation flask of a little ethyl hydrogen tartrate; but the addition of this compound to a purified sample did not prevent the yellow colour from appearing. It seems more probable that the inhibiting impurity is water and that the yellow coloration may be due to the reversible formation of a yellow anhydride, possibly a member of the keten class. The formation of this yellow anhydride would then be, like the formation of a white fume of sulphur trioxide on heating concentrated sulphuric acid, a sign of the absence of all but small traces of water.

Determinations of Freezing Point.

As a result of the very great viscosity of the ester, the determination of the freezing point was more difficult than in the case of the majority of organic compounds. Relatively large quantities of material were used in order to secure a satisfactory equilibrium of

temperature between solid and liquid, and the actual mass taken for each determination was seldom less than 500 grams. In making a measurement, the freshly distilled sample was cooled in ice, inoculated with a few crystals, and stirred vigorously; the maximum temperature was noted and the experiment was then repeated, but after the initial cooling the sample was now surrounded by water at a temperature about 1° below the maximum previously noted, in order that the temperature at which the liquid and solid were in equilibrium might be influenced to the smallest possible extent by external heating or cooling. Since most of the samples tested were substantially pure, the extent to which crystallisation proceeded was not important.

We have obtained some indications that ethyl tartrate may perhaps be dimorphous, like methyl tartrate, since from time to time we have observed freezing points substantially below those which we expected to find in view of the purity of the sample under examination. Thus, the low melting point, 6°, of the first sample received from Holland, in marked contrast with its high rotatory power, 55·68° (which should correspond with a melting point of 16° or more), may perhaps be explained in this way. Again, we have seen a very large crystal, perhaps 3 × 1½ cm., which had grown on the surface of a sample of pure tartrate (m. p. about 18·5°) go to pieces and redissolve at a room temperature of about 13°. These observations have, however, not been frequent, and, in view of the extreme difficulty of persuading the liquid to crystallise without inoculation, are beyond the range of systematic experiment. Although, therefore, we have very good grounds for suspecting that ethyl tartrate is dimorphous, we have not been able to obtain a direct experimental verification of our suspicions.

A remarkable change of freezing point which cannot be attributed to dimorphism was observed on exposing the purified ester to the high vacuum of a Langmuir pump in a vessel containing phosphoric oxide. Under these conditions the compound gave off bubbles (perhaps of alcohol or water-vapour) and liquefied, although the temperature of the room was below the original melting point of the crystals. In this experiment the melting point actually fell from 18·6° to 12·7°, and more than half of the solid melted, as a result of exposure under very low pressure in presence of phosphoric oxide. Subsequent exposure in presence of 50 per cent. sulphuric acid, giving a vapour pressure of about 3 mm. of water-vapour, or of alcohol, did not cause the liquid to become solid again, and we are therefore unable to state which of these compounds was eliminated by the phosphoric oxide.

Determinations of Density.

The density of the viscous ester was determined in a pyknometer with a capillary neck. It was filled by means of the apparatus devised by Wade and Merriman (T., 1912, **101**, 2429) for measuring the density of pure liquids, free from air and without any risk of absorption of moisture. The level of the liquid was adjusted roughly when the pyknometer had stood at constant temperature in a thermostat for three hours; after a further period of half an hour the level of the liquid was again adjusted, and the neck of the flask was cleaned with cotton wool moistened with ether; the correctness of the adjustment was checked by observing the meniscus again after the pyknometer had remained in the thermostat another half hour. The pyknometer was calibrated by filling it with air-free water at the same temperature. The results of the observations were as follow:

$$D_{4^\circ}^{20^\circ} = 1{\cdot}2028; \quad D_{4^\circ}^{25^\circ} = 1{\cdot}1980; \quad D_{4^\circ}^{34{\cdot}8^\circ} = 1{\cdot}1895.$$

Previous observations have given the values

$D_{4^\circ}^{20^\circ}$ 1·2059 (Pictet, *Jahresberichte*, 1882, 856);
$D_{4^\circ}^{20^\circ}$ 1·1989 (Landolt, *Annalen*, 1877, **188**, 324);
$D_{4^\circ}^{20^\circ}$ 1·2036, $D_{4^\circ}^{40^\circ}$ 1·1840 (Winther, *Z. physikal. Chem.*, 1902, **41**, 174).

Determinations of Viscosity.

The absolute measurement of very high viscosities is a problem which has been studied but little. Sheppard (*J. Ind. Eng. Chem.*, 1917, **9**, 523) and Jacobs (T., 1920, **117**, 473) have used the falling-sphere viscosimeter, but in our experiments we have followed Bingham (*J. Ind. Eng. Chem.*, *1914*, **6**, *233*; *Bull. Bureau of Standards, U.S.A.*, 1918, **14**, [*I*], 60), who has made a careful study of the Ostwald viscosimeter for media of high viscosity and has given absolute values for a series of strong solutions of sucrose. In our experiments, the viscosimeter had a capillary tube 12·2 cm. in length and approximately 0·1 cm. radius, the volume of liquid passing through the capillary being 12·1 c.c. Special precautions were taken to prevent the absorption of moisture by the liquid both during the filling and during the measurements. The time of flow was measured for five independent fillings of the viscosimeter and was observed, as a rule, three times for each sample at intervals of half an hour. The times were compared with those of a 60 per cent. solution of dried sucrose, the strength of which was found to be 60·01 per cent. by the polarimeter as compared with 60·05 per cent. by direct weighing. The times of flow at 19·96° were as follow:

Ethyl Tartrate.

(i) 1467·6	(ii) 1459·0	(iii) 1467·0	(iv) 1460·0	(v) 1464·0
1467·4	1459·8	1467·2		1460·4
1468·6	1459·8	1460·0		1460·6

Average time 1463·5 secs.

Sucrose (60 *per cent. by weight*).

(i) 347·8	(ii) 349·8	(iii) 347·4	(iv) 348·4
347·8	348·0	347·0	348·4
346·8	345·4	346·8	

Average time, 347·9 secs.

The times of flow, repeated at intervals over a period of twenty-four hours in one series of experiments, were as follow :

	0	0·5	1	4	8·5	12	24 hrs.
Ethyl tartrate	1467·6	1467·0	1468·0	1467·0	1465·0	1460·2	1450·4
Sucrose (60 per cent.)	350·4	349·6	350·2	348·4	—	—	343·3

Although the times recorded at the end of twenty-four hours are a few seconds lower, the ratio 1450·4/343·3 = 4·225 agrees very closely with the ratio 1463·5/347·9 = 4·207 of the average times set out above.

It will be seen that the viscosity of the ester is more than four times as great as that of the strongest sugar-solution used by Bingham. The correction for kinetic energy (Hoskins, *Phil. Mag.*, 1909, [vi], **17**, 503) was calculated to be only 0·00016 *C.G.S.* unit for the sugar solution and 0·000036 unit for the ester, and was negligible in both cases. The density of the sugar solution was 1·28644, whilst that of the tartrate was 1·2028 at 20°. Taking Bingham's value $\eta = 56{\cdot}5$ for 60 per cent. sucrose at 20°, the absolute viscosity of the ester at 20° is found to be $\eta = 221{\cdot}7$ centipoises or 2·217 *C.G.S.* units.

Refractive Indices.

The refractive index was determined with a Pulfrich refractometer made by Hilger, which was provided with a water-jacket round the liquid in addition to the usual tube dipping into the liquid (compare Lowry, *Proc. Opt. Convention*, 1912, II, 292). The instrument had been calibrated to give readings for the principal lines in the arc spectra of mercury and cadmium in addition to the usual sodium and hydrogen lines. The instrument was arranged so that the two constituents of the yellow sodium and mercury doublets could be seen separately, but readings were taken only of the less refrangible constituents. The results obtained were as follow :

TABLE I.

Refractive Indices of Ethyl Tartrate at 20°.

Line.	Wave-length.	Re-fractive index.	Line.	Wave-length.	Re-fractive index.
Cadmium red	6438	1·44481	Cadmium green	5086	1·45082
Sodium yellow	5896	1·44677	Cadmium blue	4800	1·45269
Mercury yellow	5790	1·44722	Cadmium dark blue	4678	1·45331
Mercury green	5461	1·44873	Mercury violet	4359	1·45659

These values can be plotted out as a smooth curve, but this is not reproduced in the paper.

TABLE II.

Rotatory Dispersion in Ethyl Tartrate at 20°.

(*a*) *Visual Readings.* $\alpha = \frac{180\cdot462}{\lambda^2 - 0\cdot03} - \frac{149\cdot216}{\lambda^2 - 0\cdot056}$ $[\alpha] = \frac{25\cdot005}{\lambda^2 - 0\cdot03} - \frac{20\cdot678}{\lambda^2 - 0\cdot056}$

Wave-length. λ × 10000.	Rotations in 6-dcm. tube. Obs.	Calc.	Specific rotations. Obs.	Calc.	Diff.
Li 6707·8	49·60°	49·60°	6·87°	6·87°	±
Cd 6438·5	53·30	53·27	7·38	7·38	±
Zn 6362·3	53·65	53·65	7·43	7·43	±
Na 5893·0	56·45	56·46	7·82	7·82	±
Hg 5790·7	56·84	56·81	7·87	7·87	±
Cu 5782·2	56·82	56·85	7·87	7·87	±
Hg 5769·6	56·90	56·89	7·88	7·88	±
Cu 5700·2	56·88	57·03	7·88	7·90	−0·02
Hg 5460·7	56·86	56·75	7·87	7·86	+0·01
Cu 5218·2	54·93	54·91	7·61	7·61	±
Cu 5153·3	53·98	54·03	7·48	7·48	±
Cu 5105·5	53·15	53·30	7·36	7·38	−0·02
Cd 5085·8	53·00	52·91	7·34	7·33	+0·01
Zn 4810·5	45·11	45·31	6·25	6·28	−0·03
Cd 4799·9	44·88	44·87	6·22	6·22	±
Zn 4722·2	41·52	41·50	5·75	5·75	±
Cd 4678·2	39·34	39·42	5·45	5·46	−0·01
Hg 4358·3	14·35	14·30	1·98	1·98	±

(*b*) *Photographic Readings.*

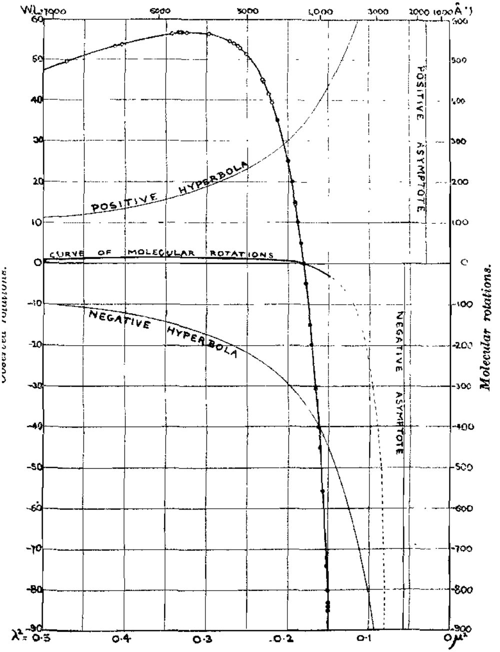
Wave-length. λ × 10000.	Rotations Obs.	Calc.	Specific rotations Obs.	Calc.	Diff.
Fe 4603	35·0	35·0	4·9	4·9	±
Fe 4475	25·0	25·5	3·5	3·5	±
Fe 4415	20·0	20·1	2·8	2·8	±
Fe 4359	15·0	14·3	2·1	2·0	+0·1
Fe 4315	10·0	9·3	1·4	1·3	+0·1
Fe 4271	5·0	3·6	0·7	0·5	+0·2
Fe 4240	0·0	0·6	0	0·1	+0·1
Fe 4210	− 5·0	− 5·0	− 0·7	− 0·7	±
Fe 4148	−15·0	−15·3	− 2·1	− 2·1	±
Fe 4119	−20·0	−20·3	− 2·8	− 2·8	±
Fe 4071	−30·5	−30·1	− 4·2	− 4·2	±
Fe 4005	−45·0	−45·1	− 6·2	− 6·2	±
Fe 3967	−55·5	−55·0	− 7·7	− 7·7	±
Fe 3900	−74·0	−74·7	−10·3	−10·4	−0·1
Fe 3889	−80·0	−78·2	−11·1	−10·8	+0·3
Fe 3872	−83·0	−83·9	−11·5	−11·6	−0·1
Fe 3868	−85·0	−85·2	−11·8	−11·8	±
Fe 3860	−88·0	−88·1	−12·2	−12·2	±

Measurements of Rotatory Dispersion.

The optical rotatory power of the pure ester was measured at 20° for a series of eighteen lines, with an eyepiece, and for eighteen

FIG. 1.

Rotatory dispersion in ethyl tartrate.



lines in the dark-blue, violet, and ultra-violet regions by a photographic method. The visual readings have been recorded to two decimal places, but except in the yellow and green the second

decimal is of very little value; the specific rotations, which are about seven times smaller, and are also given to two decimals, show much more clearly the degree of accuracy that is claimed for these observations. In the same way, in the photographic readings, the analyser was set to exact degrees, but the accuracy of the reading is certainly not closer than 0·5°; the single decimal shown in the specific rotations therefore again corresponds closely with the limit of experimental error.

Fig. 1 shows the curve of observed rotations, ranging from a positive maximum of 57° in the green to a negative value of − 88 in the last photographic reading. The figure also shows, plotted against λ^2, the curve of molecular rotations, in which the anomalies of maximum, reversal of sign, etc., are clearly seen, together with the two rectangular hyperbolas of which this complex curve is the algebraic sum. In our opinion, these two curves represent the simple rotatory dispersions of two isodynamic constituents of the ester, the constitution of which we have not yet ascertained.

Summary.

1. Ethyl tartrate, purified by distillation, freezing, and redistillation in the vacuum of a Langmuir pump, freezes at 18·7°, and gives α_{5461} + 56·9° in a 6-dcm. tube at 20°, $[\alpha]_{5461}$ + 7·87°. The density of the ester at 20° is 1·2028, and its viscosity 2·217 *C.G.S.* units.

2. The rotatory dispersion of the ester at 20° is given accurately by the formulæ

$$\alpha = \frac{180{\cdot}462}{\lambda^2 - 0{\cdot}03} - \frac{149{\cdot}216}{\lambda^2 - 0{\cdot}056}; \quad [\alpha] = \frac{25{\cdot}005}{\lambda^2 - 0{\cdot}03} - \frac{20{\cdot}678}{\lambda^2 - 0{\cdot}056}$$

where α is for a 6-dcm. column.

3. When sufficiently purified, the ester becomes yellow on heating perhaps as a result of a reversible dehydration; the pure ester also appears to decompose at atmospheric temperatures when in a high vacuum in presence of phosphoric oxide.

This work was begun at Guy's Hospital Medical School and completed at Cambridge. We are indebted to the Department of Scientific and Industrial Research for grants with the help of which the experimental work now described was carried out.

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LXIII.—*Colouring Matters from 1:2:4:5-Tetrahydroxybenzene and Related Substances.*

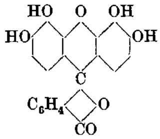
By DHIRENDRA NATH MUKERJI.

SOME studies have already been made in this laboratory on the change in the colour of dyes of various groups produced by multiplying the number of auxochromes (Medhi and Watson, T., 1915, **107**, 1581; Meek and Watson, T., 1916, **109**, 544; Ghosh and Watson, T., 1917, **111**, 815). It seemed of considerable interest to prepare from tetrahydroxybenzene as many dyes as possible, such as the phthalein, the benzein, and the fluorone, in the same way as such dyes have been prepared from resorcinol, pyrogallol, etc., as this would help in studying the effect of multiplying auxochromes in these groups of dyes.

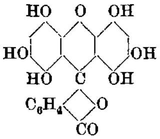
Unfortunately, the preparation in any quantity of 1 : 2 : 4 : 5-tetrahydroxybenzene, which is the only one known in the pure and free state, has proved a very laborious business. At first sight the simplest method of preparation seemed to be by the action of aniline on *p*-benzoquinone yielding dianilino-*p*-benzoquinone, which on hydrolysis yields the dihydroxyquinone, a substance readily reduced to 1 : 2 : 4 : 5-tetrahydroxybenzene (Wichelhaus, *Ber.*, 1872, **5**, 851; Nietzki and Schmidt, *ibid.*, 1888, **21**, 2377; Kehrmann, *ibid.*, 1890, **23**, 903). It was, however, found that hydrolysis of the dianilinoquinone gave an exceedingly small yield of the dihydroxyquinone, and it was therefore necessary to adopt the more laborious preparation from resorcinol *via* diacetylresorcinol, diacetyldinitroresorcinol, dinitroresorcinol, the tin double salt of diaminoresorcinol dihydrochloride, diaminoresorcinol dihydrochloride, di-iminoresorcinol, the potassium salt of dihydroxy-*p*-benzoquinone, and dihydroxy-*p*-benzoquinone to tetrahydroxybenzene (Typke, *Ber.*, 1883, **16**, 555; Nietzki and Schmidt, *ibid.*, 1888, **21**, 2374). At first, the yield of the dinitro-derivative from the diacetyl derivative was very poor, and it was necessary to study the conditions of nitration. It was found possible to increase the yield of the dinitro-derivative from 20 per cent. (Typke's yield) to 40—45 per cent. if the nitration was effected between 10° and 15° and acid of *d* 1·48 was used. It was also found that at a later stage, namely, the reduction of the dihydroxyquinone to tetrahydroxybenzene, the yield could be improved by substituting sulphur dioxide as a reducing agent in place of tin and hydrochloric acid as described in the original preparation. But, in spite of these two improvements in yield, it was found that when the nine stages in

the preparation had been carried through, the yield of tetrahydroxy benzene, reckoned on the weight of resorcinol taken, amounted only to 1—1·5 per cent.

The tetrahydroxybenzenephthalein (hexahydroxyfluoran) has been prepared and its hexa-acetyl derivative obtained in the pure condition. The preparation of the pure dyestuff is difficult and the yield unsatisfactory on account of its solubility. It dissolves in potassium hydroxide solution with a magenta colour. The dyeing properties and the absorption spectrum of this dye have not yet been studied, but it is contrary to expectation that it dissolves in the alkali with only a magenta colour. Gallein, which dissolves in potassium hydroxide solution with a blue colour (Bayer, *Ber.* 1871, 4, 457, 663), contains two benzene nuclei with two hydroxy groups in the *ortho*-position to one another in each.



Gallein.



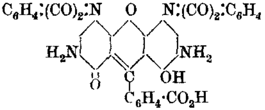
1 : 2 : 4 : 5 : 7 : 8-*Hexahydroxyfluoran*

The new dyestuff has three hydroxyl groups in the 1 : 2 : 4-positions in each nucleus, and from analogy with the anthraquinone group, we expected it to have a deeper colour than gallein (compare alizarin and purpurin; 1 : 2 : 5 : 6-tetrahydroxyanthraquinone and 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone [anthracene blue W.R.]; alizarin cyanin and anthracene blue W.R.).

Attempts to prepare the benzein from tetrahydroxybenzene and benzotrichloride were not successful. Condensation with formaldehyde gave the expected methylenebistetrahydroxybenzene, but in very poor yield. Condensation of tetrahydroxybenzene with nitrosodiomethylaniline did not yield anything inviting.

It was thought of interest to study the phthalein condensation with the diaminoresorcinol, which is an intermediate product in the preparation of tetrahydroxybenzene, and is more easily obtained than the latter substance. It was thought that if the corresponding phthalein were easily obtained it might be possible to convert the amino-groups into hydroxyl groups and thus obtain the phthalein of tetrahydroxybenzene by another method and perhaps in better yield. 4 : 6-Diaminoresorcinol dihydrochloride, however, condenses with phthalic anhydride in the presence of zinc chloride to a colourless substance, which is probably a diphthalyl derivative of diamino-

resorcinol, each of the amino-groups being converted into the phthalimino-group, and similar is the case with 2 : 4-diaminophenol. With concentrated sulphuric acid, the condensation of the diaminoresorcinol gives a dye which dissolves in potassium hydroxide solution with a fine blue colour and gives beautiful, blue-black shades on chrome-mordanted wool. It is not, however, easy to prepare it pure in any quantity and its constitution has not yet been definitely determined, although the percentage of nitrogen contained in it agrees with that required by the diphthalyl derivative of the corresponding phthalein having the following formula:



At a later time the substance may prove of interest in the study of the joint effect of amino- and hydroxyl groups on the colour of dyes, a problem which is, however, at the present time rather too complicated to be tackled.

Dinitrosoresorcinol (resorcin green) is very easily obtained in good yield from resorcinol, and it was hoped that diaminoresorcinol and thence tetrahydroxybenzene could be obtained from it. But attempts to prepare diaminoresorcinol from it were unsuccessful.

As the preparation of tetrahydroxybenzene in any quantity proved so very laborious, it was decided to work in a somewhat different direction and prepare from hydroxyquinol, pyrogallol, phloroglucinol, and 2 : 4-diaminophenol various dyes not hitherto isolated, which, on account of their containing several auxochromes, will ultimately prove of interest in the study of the general problem of the effect of the number, nature, and position of auxochromes on the colour of the containing dyes. The following new colouring matters have been prepared:

Triphenylmethane Dyes.—4′ : 4″-Tetramethyldiamino-2 : 5-dihydroxyfuchsone—blue-black in alkali; dyes greenish-black shades on chrome.

4′ : 4″ - Tetramethyldiamino - 2 : 6 - dihydroxyfuchsone — bluish-violet in alkali; dyes blue-black shades on chrome.

Fluorone Dyes.—4′-Dimethylamino-2 : 3 : 7-trihydroxy-9-phenylfluorone—reddish-violet in alkali; dyes reddish-violet shades on chrome.

4′-Dimethylamino-1 : 3 : 8-trihydroxy-9-phenylfluorone — orange in alkali; dyes orange shades on chrome.

2 : 4 : 5 : 7-Tetra-amino-4′-dimethylamino-9-phenylfluorone trichloride—brownish-yellow in acids; dyes greyish-black shades on chrome.

The problem of the effect of introducing auxochromes into three different benzene nuclei is obviously a complicated one, and it is even more complicated when, as in the above cases, some of the auxochromes are basic and others phenolic. It would be useless to discuss the above cases until many other dyes of these groups shall be available.

The very simple dye benzeneazohydroxyquinol had apparently not previously been prepared. The preparation was of interest, as the dye was expected to have a deeper colour than benzeneazoquinol, benzeneazocatechol, or benzeneazopyrogallol. It, however, dissolves in alkali with only an orange-red colour and gives brownish-red shades on chrome.

Experimental.

1 : 2 : 4 : 5 : 7 : 8-*Hexa-acetoxyfluoran*, $\begin{matrix} C_6H_4 \\ CO{\cdot}O \end{matrix}\!>\!C\!<\!\begin{matrix} C_6H(OAc)_3 \\ C_6H(OAc)_3 \end{matrix}\!>\!O.$

An intimate mixture of tetrahydroxybenzene (1 gram) and phthalic anhydride (0·8 gram) was heated at 100° and powdered zinc chloride (0·5 gram) added. After being heated at 150—160° for two to three hours with constant stirring, the mixture solidified. The product was powdered and washed with concentrated hydrochloric acid, which removed most of the zinc chloride, leaving the yellowish-green dyestuff behind. The dyestuff dissolves in alkali with a beautiful magenta colour. It is very soluble in alcohol or acetone, sparingly soluble in cold water, and insoluble in benzene or ether. Repeated attempts to crystallise the substance having proved ineffectual, it was acetylated by heating it with fused sodium acetate (1 part) and acetic anhydride (5 parts) in a sealed tube at 150—160° for one hour. The product was treated with 5 c.c. of glacial acetic acid and poured into water, which precipitated the acetyl compound as a pale brown, amorphous mass. This was crystallised from dilute alcohol and obtained in small, colourless needles, which did not melt at 300°. The substance is soluble in alcohol or acetone and insoluble in ether (Found: C = 59·31; H = 3·91. $C_{32}H_{24}O_{15}$ requires C = 59·25; H = 3·91 per cent.).

On deacetylation, the pure dyestuff was obtained, which dissolved in alkali with a brilliant magenta colour. The quantity available being very small, the analysis could not be attempted.

Methylenebis-2 : 3 : 5 : 6-tetrahydroxybenzene,
$C_6H(OH)_4\cdot CH_2\cdot C_6H(OH)_4$.

A mixture of the tetrahydroxybenzene (0·4 gram), dissolved in 20 c.c. of dilute hydrochloric acid (1 : 10) and 4 c.c. of 4 per cent. formaldehyde solution, was kept for twelve hours at the ordinary temperature, when the methylene compound separated in a crystalline condition. It was recrystallised from acetone and obtained in colourless needles which did not melt at 300°. The substance is sparingly soluble, in alcohol or acetone, and insoluble in benzene or ether (Found: C = 52·88; H = 3·94. $C_{13}H_{12}O_8$ requires C = 52·70; H = 4·05 per cent.).

(?) *Diphthalyl Derivative of* 2 : 4 : 5 : 7-*Tetra-amino-*
1 : 8-*dihydroxyfluoran*, $C_{36}H_{20}O_9N_4$.

A finely powdered mixture of 1·5 grams of phthalic anhydride and 1 gram of 4 : 6-diaminoresorcinol dihydrochloride was heated with 3 c.c. of concentrated sulphuric acid at 150—160° for two to three hours and finally at 180—190° for one hour. The solution of the crude product in boiling water having been filtered, the dyestuff was salted out with sodium chloride and purified by dissolving it in alkali and precipitating it with glacial acetic acid. The *substance dissolves with a beautiful blue colour in alkali and with a* reddish-violet colour in hydrochloric acid. It dyes chrome-mordanted wool brilliant blue-black. It does not melt at 300° (Found: N = 8·31. $C_{36}H_{20}O_9N_4$ requires N = 8·58 per cent.).

4 : 6-*Diphthaliminoresorcinol*, $C_6H_2(OH)_2[N\colon(CO)_2\colon C_6H_4]_2$.

Two grams of the diaminoresorcinol hydrochloride were intimately mixed with 1·5 grams of phthalic anhydride and heated in an oil-bath while a slow current of dry carbon dioxide was passed over the mixture to prevent oxidation of the amino-compound. The temperature was raised to 120° and 1 gram of powdered zinc chloride added. The whole mass was well stirred and the temperature maintained at 150—160° for one and a half hours. The condensation product was washed with cold dilute hydrochloric acid and then with boiling water. It crystallised in needles from dilute acetic acid and did not melt at 300° (Found: N = 7·19. $C_{22}H_{12}O_6N_2$ requires N = 7·00 per cent.).

2 : 4-*Diphthaliminophenol*, $C_6H_3(OH)[N\colon(CO)_2\colon C_6H_4]_2$.

Equivalent proportions of the diaminophenol hydrochloride and phthalic anhydride were treated exactly as described above. The

substance was crystallised from a mixture of acetic acid and water and obtained in colourless needles, which melted and decomposed at 247° (Found: N = 7·41. $C_{22}H_{12}O_5N_2$ requires N = 7·29 per cent.).

4'-Dimethylamino-2 : 3 : 7-trihydroxy-9-phenylfluorone.

A solution of 1 gram of *p*-dimethylaminobenzaldehyde and 2 grams of hydroxyquinol in 12 c.c. of 50 per cent. alcohol was treated with 1·5 c.c. of concentrated sulphuric acid (*d* 1·84) and kept at the ordinary temperature for three days. It was then boiled on the water-bath for half an hour and allowed to cool, when the sulphate of the dyestuff crystallised out in beautiful orange, shining plates. This was filtered off, washed with alcohol, and dried in the steam oven. It sintered at 250°, but did not melt at 300°. The free base was liberated by boiling the sulphate with dilute aqueous ammonia. The dyestuff is sparingly soluble in the common organic solvents, but dissolves readily in alkali with a reddish-violet colour, and imparts the same shade to chrome-mordanted wool. It does not melt at 300° [Found: for the sulphate, H_2SO_4 = 28·42. $(C_{21}H_{17}O_5N)_2,3H_2SO_4$ requires H_2SO_4 = 28·82 per cent. Found: for the base, C = 69·23; H = 5·47. $C_{21}H_{17}O_5N$ requires C = 69·44; H = 5·23 per cent.].

4'-Dimethylamino-1 : 3 : 8-trihydroxy-9-phenylfluorone.

As in the last experiment, *p*-dimethylaminobenzaldehyde was condensed with phloroglucinol in presence of sulphuric acid. The sulphate crystallised from dilute sulphuric acid in small, brownish-red plates which decomposed at 255°. The dyestuff was obtained from the sulphate by boiling it with a very dilute solution of ammonium hydroxide. It is easily soluble in alcohol or acetone, and is obtained from hot dilute alcohol as an orange, amorphous powder which does not melt at 300°. It dissolves in alkali with an orange colour, and imparts the same shade to chrome-mordanted wool [Found: for the sulphate, H_2SO_4 = 28·78. $(C_{21}H_{17}O_5N)_2,3H_2SO_4$ requires H_2SO_4 = 28·82 per cent. Found: for the base, C = 69·34; H = 5·41. $C_{21}H_{17}O_5N$ requires C = 69·44; H = 5·23 per cent.].

2 : 4 : 5 : 7-*Tetra-amino-4'-dimethylamino-9-phenylfluorone Trichloride.*

A mixture of 1 gram of *p*-dimethylaminobenzaldehyde and 2·2 grams of 2 : 4-diaminophenol hydrochloride was dissolved in 10 c.c.

of 50 per cent. alcohol with 3 c.c. of concentrated hydrochloric acid and the solution was left for twelve hours at the ordinary temperature. The fine orange-yellow, crystalline mass that separated was filtered, washed with absolute alcohol, and recrystallised from a mixture of alcohol and dilute hydrochloric acid, and was obtained in deep yellow needles which became orange when dried at 100°. The substance decomposes at 245—252°. It is easily soluble in water or dilute mineral acids, but is insoluble in alkali. It dyes chrome-mordanted wool greyish-black (Found: N = 14·73; Cl = 22·59. $C_{21}H_{24}ON_5Cl_3$ requires N = 14·94; Cl = 22·73 per cent.).

4′ : 4″-Tetramethyldiamino-2 : 5-dihydroxyfuchsone,
$O:C_6H_2(OH)_2:C(C_6H_4{\cdot}NMe_2)_2$.

Three grams of Michler's ketone were heated with 3·5 c.c. of phosphoryl chloride (*d* 1·69) for ten to fifteen minutes on a water-bath. To the green melt two grams of finely powdered hydroxyquinol were gradually added with constant stirring. The heating on the water-bath was continued for two more hours, after which the mixture was dissolved in 30 per cent. acetic acid and the dyestuff precipitated from the solution by the addition of sodium acetate. It was purified by dissolving it in sodium carbonate solution and precipitating with glacial acetic acid, and was thus obtained as a deep violet powder which did not melt at 300°. The substance dissolves in alkali carbonate with a blue-black colour and gives a greenish-black shade on chrome-mordanted wool (Found: N = 7·30. $C_{23}H_{24}O_3N_2$ requires N = 7·44 per cent.).

4′ : 4″-Tetramethyldiamino-2 : 6-dihydroxyfuchsone.

This was prepared by the preceding process, phloroglucinol being employed instead of hydroxyquinol. The dyestuff was obtained as a brownish-violet powder which did not melt at 300°. It dissolves in alkali with a fine bluish-violet colour and gives a blue-black shade on chrome-mordanted wool (Found: N = 7·68. $C_{23}H_{24}O_3N_2$ requires N = 7·44 per cent.).

Benzeneazohydroxyquinol, $C_6H_5{\cdot}N:N{\cdot}C_6H_2(OH)_3$.

One gram of aniline was diazotised, treated with an alcoholic solution of 1·3 grams of hydroxyquinol, and the mixture, after being well stirred for five minutes, was treated with sodium acetate, which precipitated the azo-compound as a brownish-red mass. The whole mass was well stirred for half an hour and kept over-night. It

was filtered, washed, and the azo-compound obtained from hot dilute alcohol in small brownish-red needles which melted at 179—180°. The substance dissolves in alkali with an orange-red colour and gives a brownish-red shade on chrome-mordanted wool (Found: N = 11·92. $C_{12}H_{10}O_3N_2$ requires N = 12·17 per cent.).

In conclusion, the author expresses his sincere thanks to Professor E. R. Watson for his kind encouragement and valuable suggestions.

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LXIV.—*The Reaction between Iodine and Sulphurous Acid.*

By ROBERT MILROY MACAULAY.

IT is stated in most text-books of analytical chemistry that in the estimation of sulphurous acid by means of iodine correct results are obtained only when the sulphurous acid has been added to the iodine; and that when iodine solution has been added to sulphurous acid the results are invariably low.

The following experiments were undertaken with the object of forming a decision in respect of the several explanations that have been given of this phenomenon, and of determining whether the complex formed between sulphur dioxide and hydrogen iodide (Péchard, *Compt. rend.*, 1900, **130**, 1188) has any influence on the reaction.

EXPERIMENTAL.

The solutions of sulphurous acid employed were prepared by passing sulphur dioxide from a siphon into air-free water until the solutions were of the desired strength.

In the titrations, stoppered bottles were employed; and when the reaction was almost complete, the stopper was inserted, and the bottle shaken.

Since the concentration of the sulphurous acid solution quickly decreased on keeping, only the experiments performed at the same time gave comparable results. These are recorded in the same horizontal line in Table I.

TABLE I.

Exp.	C.c. of $N/10$-iodine.	C.c. of H_2SO_3 required.	Conc. of SO_2. Grams per litre.	C.c. of H_2SO_3.	C.c. of $N/10$-iodine required.	Conc. of SO_2. Grams per litre.
1	10	19·00	1·673	20	9·95	1·581
2	,,	20·50	1·551	,,	9·75	1·550
3				,,	26·30	
4				,,	,,	
5	20	21·00	3·080	,,	19·05	3·081
6	,,	14·90	4·320	,,	26·80	4·313
7	,,	15·00	4·291	,,	26·45	4·258
8	,,	14·95	4·293	,,	26·70	4·296
9	,,	,,	,,	,,	,,	,,

Results similar to that of experiment 2 were frequently obtained, especially when the iodine solution was added quickly. When stronger solutions of sulphurous acid than the above were employed, concordant results were not obtained, addition of the iodine solution to the sulphurous acid invariably giving lower values than those obtained by inverting the order of the addition.

When the sulphurous acid was approximately $N/5$ or stronger, a yellow coloration was produced on adding $N/10$-iodine. This coloration was due, not to free iodine (Péchard, *loc. cit.*; compare also Fox, *Z. physikal. Chem.*, 1902, **41**, 458), but to the formation of the compound SO_2,HI. On adding more iodine, the colour deepened up to a point, and then became paler again, the solution being colourless when the titration was nearly completed. Thus it would appear that the compound SO_2,HI did not interfere with the reaction, the sulphurous acid being oxidised by the iodine in the usual way. When more sulphurous acid was added to the liquid, the yellow coloration again developed. The solution was then kept for twenty-four hours, but no separation of sulphur took place. The yellow colour deepened on the addition of hydriodic acid, but sulphur was not deposited. This disproves Volhard's theory (*Annalen*, 1888, **242**, 93) of the reduction of sulphurous acid to sulphur in solutions up to about $N/5$.

Experiments 3 and 4 were performed under comparable conditions in an atmosphere of carbon dioxide; in the former, 5 c.c. of hydriodic acid were added before titrating.

A solution of sulphur dioxide in air-free water was stored in a bottle filled with carbon dioxide, oil being placed on the surface of the liquid to prevent loss of sulphur dioxide by evaporation. An atmosphere of carbon dioxide was maintained in the bottle, and in the burette, with which the bottle was connected. An attachment was made to the nozzle of the burette, so that the sulphurous acid was delivered at the bottom of the receiving vessel. Titrations performed in an atmosphere of carbon dioxide gave the results

recorded in experiment 5. The erratic results often obtained under other experimental conditions would therefore appear to be due either to loss of sulphur dioxide by evaporation or to oxidation of sulphurous acid by air.

These suppositions were tested by means of titrations made with (experiment 6) and without (experiment 7) the burette attachment; in both cases the bottles were filled with carbon dioxide. In experiment 7 the results differed by approximately 1 per cent., and were lower than those obtained in experiment 6, which agreed within the limits of experimental error. Thus it would appear that the loss of sulphur dioxide by evaporation is appreciable.

The titrations were repeated, the bottles being filled with air. The burette attachment was employed (experiment 8).

At the same time, the experiments were repeated, the bottles heing first filled with carbon dioxide (experiment 9).

From these results it is apparent that the erratic and low results obtained by titrating sulphurous acid with iodine are due wholly to loss of sulphur dioxide by evaporation. It was also observed that the stronger the sulphurous acid, the greater was the difference between the results of the two methods of titration; and the more quickly the iodine was added, the smaller was the difference.

In many cases the titration of sulphurous acid with iodine appeared to be finished, the yellow colour (due to free iodine) persisting when the bottle was merely rotated. On inserting the stopper, however, and shaking the bottle, the colour disappeared, and an appreciable amount of iodine solution had still to be added before the oxidation of the sulphurous acid was completed. This showed the presence of an appreciable quantity of sulphur dioxide in the space above the liquid in the bottle.

The foregoing experiments were repeated with sulphurous acid of different strengths; the values given above are typical results.

Sodium Sulphite Solution.

When iodine solution is added to sodium sulphite solution, lower results are obtained than in the reverse process. In this case the lowness of the results appears to be due to oxidation of sodium sulphite by air. This was demonstrated by performing the titrations in an atmosphere of (1) air, (2) carbon dioxide.

In the former case the result obtained by adding the iodine solution to the sodium sulphite solution was lower than that obtained by adding the sodium sulphite to the iodine.

In case (2) similar results were obtained by both methods, and they agreed with those obtained by titrating iodine solution (acidified with hydrochloric acid) with sodium sulphite solution; and also with those obtained by an indirect titration.

In the following experiments the sodium sulphite solution was prepared by dissolving crystallised sodium sulphite in air-free water and storing the solution in a bottle connected with a two-way burette; an atmosphere of carbon dioxide was maintained in the bottle and in the burette.

1. *In an atmosphere of air.*

(*a*) 22·45 C.c. of sodium sulphite required 21·55 c.c. of *N*/10-iodine. Concentration of Na_2SO_3 = 6·049 grams per litre.

(*b*) 20·20 C.c. of *N*/10-iodine required 20·85 c.c. of sodium sulphite. Concentration of Na_2SO_3 = 6·105 grams per litre.

(*c*) 19·05 C.c. of *N*/10-iodine + 16·77 c.c. of sodium sulphite required 2·85 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·088 grams per litre.

(*d*) 15·96 C.c. of *N*/10-iodine + 14·80 c.c. of sodium sulphite + 1 gram of sodium hydrogen carbonate, titrated immediately, required 1·63 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·101 grams per litre.

(*e*) 16·10 C.c. of *N*/10-iodine + 16·20 c.c. of sodium sulphite + 1 gram of sodium hydrogen carbonate, titrated after fifteen minutes, required 0·43 c.c. of *N*/10-thiosulphate. Concentration of Na_2SO_3 = 6·096 grams per litre.

2. *In an atmosphere of carbon dioxide.*

(*a*) 22·10 C.c. of sodium sulphite required 21·42 c.c. of *N*/10-iodine. Concentration of Na_2SO_3 = 6·108 grams per litre.

(*b*) 21·25 C.c. of *N*/10-iodine required 21·95 c.c. of sodium sulphite. Concentration of Na_2SO_3 = 6·101 grams per litre.

Results 1 (*d*) and (*e*) differ from those of Rupp (*Ber.*, 1902, **35**, 3694), who states that keeping of the solution for fifteen minutes is necessary for the complete oxidation of sodium sulphite in the presence of sodium hydrogen carbonate, as the rate of oxidation of sodium sulphite is slower than that of sulphurous acid, or free sulphur dioxide. This is contrary to experience, sulphur dioxide being more easily oxidised in presence of alkali (Raschig, *Z. angew. Chem.*, 1904, **17**, 577). Addition of sodium hydrogen carbonate also seems unnecessary, since the reaction $Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$ is not reversible.

Conclusions.

Sulphurous acid is quantitatively oxidised to sulphuric acid by $N/10$-iodine, without the separation of sulphur. The intermediate formation of the yellow compound, SO_2,HI, which occurs in solutions of moderate concentration, has no influcnce on the final result.

The low results obtained when sulphurous acid is exposed to the air during the titration are due entirely to evaporation of sulphur dioxide, thc amount of atmospheric oxidation being negligible.

Sodium sulphite solution is more readily oxidised than sulphurous acid; consequently atmospheric oxidation is a disturbing factor when sodium sulphite solution is titrated with iodine. Since the reaction between sulphurous acid and iodine is not reversed under the state of dilution obtaining in volumetric analysis, the addition of sodium hydrogen carbonate to neutralise hydriodic acid, as when solutions of arsenious compounds are being titrated, is unnecessary; and since a sulphite solution is so quickly oxidised, it is not necessary to allow a time interval for such oxidation by iodine to be completed.

The author desircs to express his thanks to Professor R. M. Caven for suggesting this work, and for the interest he has taken in the matter.

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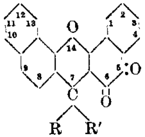
Glasgow. [*Received, January 20th,* 1922.]

LXV.—*The Oxidation of α-Dinaphthaxanthens.*

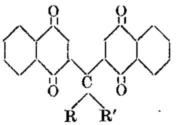
By Hemendra Kumar Sen-Gupta and Stanley Horwood Tucker.

The condensation of α-naphthol with various ketones has been investigated by one of us (Sen-Gupta, T., 1914, **105**, 399). The present communication has arisen out of an investigation of the oxidation of the products of condensation of α-naphthol with acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone respectively. In general, in the oxidation of any particular anhydro-1 : 1-dihydroxydinaphthyldialkylmethane by means of sodium dichromate in glacial acetic acid solution, there are formed simultaneously two products: one, deep orange to red, and the other a brilliant yellow.

The colour of these products suggests that they contain an ortho-quinonoid and a para-quinonoid grouping respectively, and investigation confirms this idea. Thus the orange oxidation products are readily reduced, but form unstable dihydroxy-derivatives. If, however, reduction is effected in the presence of acetylating agents, stable diacetyl derivatives can be isolated. By the action of *o*-phenylenediamine in glacial acetic acid or in alcoholic solution quinoxalines are formed. Whereas the parent anhydro-compounds form mono- and di-nitro-derivatives, the orange oxidation products form mononitro-derivatives only, indicating that one naphthalene group has become oxygenated, leaving the other still free for nitration. The alkyl groups are unaffected in the oxidation process. There is no evidence of xanthone formation. Hence the structure of the orange oxidation products may be represented by I, which



(I.)



(II.)

classes them as ortho-diketodialkyldihydro-α-dinaphthaxanthens. The nitro-group of the mononitro-derivative is therefore probably present in position 9, the quinoxaline nucleus is formed at positions 5 and 6, and the diacetyl derivative of the unstable reduction product referred to above contains its acetoxy-groups in positions 5 and 6.

5 : 6-Diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen and

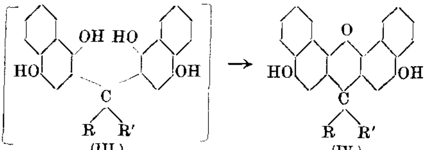
the corresponding methyl ethyl and diethyl compounds normally give mononitro-derivatives, but attempts to prepare a mononitro-derivative of *5 : 6-diketo-7-methyl-7-n-propyl-5* : 6-dihydro-α-dinaphthaxanthen by the usual method, that is, treatment of the glacial acetic acid solution of the diketo-compound with fuming nitric acid at 100°, have failed. Consequently, nitration was attempted in the *boiling* solution. No nitro-compound separated, but the mixture left, after evaporation, a crystalline residue containing phthalic acid. A similar experiment with 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen, performed in boiling glacial acetic acid, gave rise likewise to phthalic acid, but mixed with a considerable quantity of a yellow nitro-compound.

The 5 : 6-diketo-7 : 7-dialkyl-5 : *6-dihydro-α-dinaphthaxanthens* are very sensitive to light. If they are preserved in the dark, no decomposition will occur, but exposure to sunlight changes the colour from deep orange to bright scarlet. They are further characterised by high melting points and sparing solubility.

The yellow oxidation products differ notably in properties from the orange oxidation products. The yellow products cannot be nitrated; they can be recovered unchanged from fuming nitric acid. From this it may be inferred that the oxygen atoms are arranged symmetrically in the naphthalene ring systems. They do not give quinoxalines with *o*-phenylenediamine. Their colour and other properties indicate that they possess the para-quinonoid grouping, and their structure is accordingly represented by formula II, that is, they are di-2-α-naphthaquinonyldialkylmethanes.

In all their reactions these substances behave as α-naphthaquinone. Sulphur dioxide has no effect on them, but zinc dust in glacial acetic acid brings about reduction to 5 : 9-dihydroxy-7 : *7-dialkyl-α-dinaphthaxanthens*; the expected 1 : 4 : 1′ : 4′-tetrahydroxy-ββ-dinaphthyldialkylmethanes cannot be isolated. The course of the reaction is readily explained thus :

(II.) →



(III.) (IV.)

Anhydride formation is to be expected in such circumstances. The change III → IV is exemplified in numerous instances; for example, Copisarow and Weizmann (T., 1915, **107**, 880) prepared

from di-1-ethoxynaphthylphthalide the stable α-naphthaphthalein and converted this hydroxy-compound into its anhydride, α-naphthafluoran. That the final product of the reduction of di-2-α-naphthaquinonyldialkylmethane is a dihydroxy-compound (IV) is indicated by the formation of the diacetyl, dibenzoyl, and dimethyl derivatives. The diacetoxy-compounds are isomeric with the corresponding 5 : 6-diacetoxy-7 : 7-dialkyl-α-dinaphthaxanthens, prepared by the reduction and subsequent acetylation of the 5 : 6-diketo-7 : 7-dialkyl-5 : 6-dihydro-α-dinaphthaxanthens (I).

The crystals of the dihydroxy-compounds formed in glacial acetic acid solution have been measured. A close crystallographic similarity, pointing to isomorphism, exists between 5 : 9-dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen and the corresponding diethyl compound. The crystals of 5 : 9-dihydroxy-7-methyl-7-*n*-propyl-α-dinaphthaxanthen, which do not contain acetic acid, do not resemble the above.

5 : 9-Dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen reacts with chlorine to give a crystalline chloro-derivative.

With the object of elucidating the constitution of the chloro-compound prepared by one of us (Sen-Gupta, *loc. cit.*) by the action of chlorine on anhydro-β-1 : 1-dihydroxydinaphthylpropane, attempts have been made to replace the two hydroxyl groups in 5 : 9-dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen by chlorine. Thionyl chloride reacts with the compound, and there is formed a crystalline substance which contains chlorine and no sulphur; its investigation is in hand.

Finally, it may be said that the considerations adduced above prove that the anhydrodihydroxydinaphthylparaffins (Sen-Gupta, *loc. cit.*) are 7 : 7-dialkyl-α-dinaphthaxanthens, and they are designated as such in the experimental portion of this paper.

EXPERIMENTAL.

Oxidation of 7 : 7-*Dimethyl-α-dinaphthaxanthen* (*Anhydro*-β-1 : 1-*dihydroxydinaphthylpropane*), $CMe_2<^{C_{10}H_6}_{C_{10}H_6}>O$.

Sodium dichromate (25 grams) is added during twenty minutes to a warm solution of 7 : 7-dimethyl-α-dinaphthaxanthen (5 grams) in glacial acetic acid (75 c.c.), the liquid being boiled after each addition. The mixture of orange and yellow crystals which separates is washed with glacial acetic acid until the faintly red filtrate is free from chromium salts. The orange residue is 5 : 6-*diketo*-7 : 7-*dimethyl*-5 : 6-*dihydro-α-dinaphthaxanthen*. The combined filtrates are heated for two hours with more sodium dichromate (10—12

grams) and poured into water. The yellow, flocculent precipitate is ββ-*di*-2-α-*naphthaquinonylpropane*.

These two products may also be separated thus :—The mixture is dissolved in a slight excess of boiling glacial acetic acid. Before the solution has attained room temperature it is filtered from the orange crystals—which separate practically pure—and to the filtrate excess of fuming nitric acid is added and the solution maintained at 100° for half an hour. The insoluble nitro-derivative is removed, and the filtrate deposits the yellow product in a pure condition.

5 : 6-*Diketo*-7 : 7-*dimethyl*-5 : 6-*dihydro*-α-*dinaphthaxanthen* (I) crystallises from glacial acetic acid, or from pyridine diluted with water, in dark orange needles, melting at 287° (Found : C = 81·2; H = 4·7. $C_{23}H_{16}O_3$ requires C = 81·2; H = 4·7 per cent.). It is sparingly soluble in alcohol, acetone, ether, or carbon tetrachloride, but readily soluble in pyridine, benzene, nitrobenzene, or chloroform. It dissolves in concentrated sulphuric acid to form a deep bottle-green solution, which darkens to purple on heating. Bromine, added to the glacial acetic acid solution of the substance, causes, on boiling for a few seconds, the precipitation of salmon-coloured needles. These have not yet been examined.

A *mononitro*-derivative is obtained by dissolving 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen in glacial acetic acid, adding excess of fuming nitric acid, and maintaining at 100° for half an hour. The nitro-derivative, which is sparingly soluble in acetic acid, crystallises in long, yellow needles. It is very soluble in hot nitrobenzene. It shows signs of melting and decomposition at 330° (Found : N = 3·8. $C_{24}H_{15}O_5N$ requires N = 3·6 per cent.).

If, however, fuming nitric acid is added to the glacial acetic acid solution and the mixture is *boiled*, the reaction will take a different course. The solution was boiled for a quarter of an hour and then evaporated to dryness. The yellow oil thus obtained, on standing, crystallised in small, white needles, which appeared to be phthalic acid.

The Quinoxaline.—A solution of 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen (1 gram) mixed with *o*-phenylenediamine (0·8 gram) in glacial acetic acid (10 c.c.) is warmed, and the pale yellow, crystalline solid that is deposited is recrystallised from glacial acetic acid and then from alcohol in pale brown needles which melt at 251—252° (Found: C = 84·8; H = 5·0; N = 6·8. $C_{29}H_{20}ON_2$ requires C = 84·5; H = 4·9; N = 6·8 per cent.).

5 : 6-Diacetoxy-7 : 7-dimethyl-α-dinaphthaxanthen. — 5 : 6 -Diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen (1 gram) is dissolved in acetic anhydride (10—12 c.c.) and glacial acetic acid

(about 10 c.c.) by boiling, and zinc dust added until the colour is discharged. Fused sodium acetate (3 grams) is now added and the mixture boiled for some time. The acetyl derivative, isolated in the usual manner, is crystallised from glacial acetic acid or alcohol in colourless needles melting at 251—254° (Found: C = 75·7; H = 5·1. $C_{27}H_{22}O_5$ requires C = 76·0; H = 5·2 per cent.).

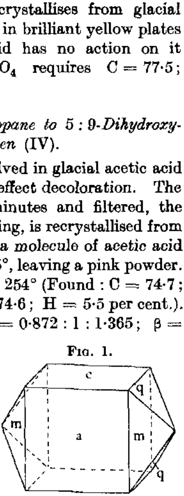
ββ-*Di-2-α-naphthaquinonylpropane* (II) crystallises from glacial acetic acid, or pyridine diluted with water, in brilliant yellow plates melting at 245—248°. Fuming nitric acid has no action on it (Found: C = 77·3; H = 4·6. $C_{24}H_{16}O_4$ requires C = 77·5; H = 4·5 per cent.).

Reduction of ββ-Di-2-α-naphthaquinonylpropane to 5 : 9-Dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen (IV).

The propane derivative (1 gram) is dissolved in glacial acetic acid (25 c.c.) and zinc dust gradually added to effect decoloration. The mixture having been boiled for a few minutes and filtered, the reduction product, which separates on cooling, is recrystallised from glacial acetic acid. The product contains a molecule of acetic acid of crystallisation, which it loses at 120—125°, leaving a pink powder. It turns faintly brown at 240° and melts at 254° (Found: C = 74·7; H = 5·5. $C_{23}H_{18}O_3,C_2H_4O_2$ requires C = 74·6; H = 5·5 per cent.).

The crystals are monoclinic; $a : b : c$ = 0·872 : 1 : 1·365; β = 99° 43′. Forms: a{100}, m{110}, c{001}, q{011}. The common habit is elongated along the b-axis and tabular parallel either to a(100), as in Fig. 1, or tabular parallel to c(001). Two small crystals, about 1 mm. in their largest dimension, were found to be measurable, and the mean angular values obtained from these are given below:

FIG. 1.



	a{100}.	m{110}.	c{001}.	q{0$\bar{1}$1}.
φ	89° 29′ (+31′)	*49° 19′	91° 1′ (−1° 1′)	7° 0′ (0° 0′)
ρ	90 0 (0° 0′)	90 0 (0° 0′)	*9 43	*54 0

The above product, containing acetic acid, is very soluble in hot alcohol, giving a violet fluorescing solution. The addition of an equal volume of hot water to this solution effects the precipitation of colourless plates, which become brown at 240° and melt at 254°, as before. The product contains one molecule of alcohol of crystallisation (Found: C = 77·3; H = 6·2. $C_{24}H_{18}O_3,C_2H_6O$ requires C = 77·3; H = 6·2 per cent.). The crystals are insoluble in light petroleum, soluble in benzene or xylene, and very soluble in ethyl

acetate. The crystals formed in xylene solution contain xylene of crystallisation; they are needle-shaped, and melt at 241—244°. Potassium hydroxide solution dissolves all three crystalline products to apple-green solutions, which become deep green on standing or on warming.

Thionyl chloride acted on 5 : 9-dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen with evolution of hydrochloric acid, but although crystalline products were obtained and shown to contain chlorine and not sulphur, no pure compound could be isolated. 5 : 9-Dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen reacts with chlorine in a boiling solution of glacial acetic acid to give pale green crystals, which melt at 242—244°.

5 : 9-*Diacetoxy-7 : 7-dimethyl-α-dinaphthaxanthen*, prepared by boiling the dihydroxy-compound with excess of acetyl chloride until a crystalline precipitate commences to separate, or with acetic anhydride and fused sodium acetate, crystallises from glacial acetic acid in needles melting at 239—241° (Found: C = 75·9; H = 5·1. $C_{27}H_{22}O_5$ requires C = 76·1; H = 5·2 per cent.).

5 : 9-*Dibenzoyloxy-7 : 7-dimethyl-α-dinaphthaxanthen* is prepared by boiling 5 : 9-dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen with sufficient benzoyl chloride to effect solution. After one minute's boiling, the solution, without addition of caustic alkali, is poured into water, and the readily precipitated dibenzoyl derivative separated. It crystallises from glacial acetic acid in pointed laminæ, which melt at 239—240°. The crystals contain one molecule of acetic acid (Found: C = 76·6; H = 5·1. $C_{37}H_{26}O_5,C_2H_4O_2$ requires C = 76·7; H = 4·9 per cent.). When heated at 140°, the crystals lose acetic acid of crystallisation, but the powder melts, as before, at 239—240° (Found: acetic acid = 9·8. $C_{37}H_{26}O_5$, $C_2H_4O_2$ requires acetic acid = 9·8 per cent.). The oven-dried product crystallises from pyridine (Found: C = 80·8; H = 4·9. $C_{37}H_{26}O_5$ requires C = 80·7; H = 4·7 per cent.).

5 : 9 - *Dimethoxy - 7 : 7 - dimethyl-α-dinaphthaxanthen.*—5 : 9 - Dihydroxy-7 : 7-dimethyl-α-dinaphthaxanthen (1 gram) is dissolved in potassium hydroxide solution (9 c.c. of 15 per cent.) and the apple-green solution treated with methyl sulphate (0·75 gram), whereupon a salmon-coloured precipitate separates; this is crystallised from amyl alcohol in pale salmon plates, which show signs of change at 280° and melt at 291° (Found: C = 80·7; H = 6·0. $C_{23}H_{22}O_3$ requires C = 81·1; H = 6·0 per cent.).

The substance decomposes when it is heated, and a vapour is evolved having a naphtholic odour. It dissolves in cold concentrated sulphuric acid to a yellow-red solution, which becomes brown on warming. It is insoluble in ethyl acetate, ethyl alcohol, or light

petroleum, slightly soluble in glacial acetic acid, and soluble in acetone, pyridine, amyl alcohol, carbon disulphide, chloroform, aniline, benzene, or nitrobenzene. It crystallises well from amyl alcohol, pyridine, or benzene.

Substance melting at 250°.—The crystals separating from a benzene solution behave abnormally. They are hard, warty, and nearly white; on drying at 120°, they fall to a powder which melts at 250°. A mixture with the above-described dimethoxy-compound melts at 243°. The investigation of the substance is being continued.

Oxidation of 7-*Methyl*-7-*ethyl*-α-*dinaphthaxanthen* (*Anhydro*-β-*dihydroxydinaphthylbutane*).

7-Methyl-7-ethyl-α-dinaphthaxanthen is oxidised with sodium dichromate in glacial acetic acid as described under the oxidation of 7 : 7-dimethyl-α-dinaphthaxanthen, and the resulting orange 5 : 6-diketo-7-methyl-7-ethyl-5 : 6-dihydro-α-dinaphthaxenthen and the yellow ββ-di-2-α-naphthaquinonylbutane are separated as in that case.

5 : 6-*Diketo*-7-*methyl*-7-*ethyl*-5 : 6-*dihydro*-α-*dinaphthaxanthen* (I) can be crystallised from glacial acetic acid, or from pyridine diluted with water, in orange needles which melt with decomposition at 276°. The crystals become scarlet when they are exposed to sunlight (Found: C = 81·4; H = 5·1. $C_{24}H_{18}O_3$ requires C = 81·4; H = 5·1 per cent.).

A *mononitro*-derivative is prepared similarly to its lower homologue; it crystallises in pale salmon-coloured prisms which melt at 301°, showing signs of change at 297° (Found: N = 3·6. $C_{24}H_{17}O_5N$ requires N = 3·5 per cent.).

The *quinoxaline* is prepared as the corresponding quinoxaline from 5 : 6-diketo-7 : 7-dimethyl-5 : 6-dihydro-α-dinaphthaxanthen. It crystallises from glacial acetic acid containing a small amount of alcohol in short, bright yellow rods, which melt at 236—241° (Found: N = 6·5. $C_{30}H_{22}ON_2$ requires N = 6·6 per cent.). In certain preparations, a bright yellow, crystalline material was obtained which melted at 225—227°. The quinoxaline is soluble in benzene, glacial acetic acid, acetone, ethyl acetate, or pyridine, slightly soluble in alcohol, and insoluble in light petroleum. It dissolves in pyridine to a red solution which exhibits a deep green fluorescence, similar in tint to that of fluorescein. The solution in ethyl acetate is yellow and shows a pale green fluorescence.

5 : 6-*Diacetoxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen* is prepared from 5 : 6-diketo-7-methyl-7-ethyl-5 : 6-dihydro-α-dinaphthaxanthen similarly to 5 : 6-diacetoxy-7 : 7-dimethyl-α-dinaphthaxanthen. It

crystallises in colourless needles which melt at 242—244° (Found : C = 76·7 ; H = 5·4. $C_{23}H_{24}O_5$ requires C = 76·4 ; H = 5·4 per cent.).

ββ-*Di*-2-α-*naphthaquinonylbutane* (II) crystallises from glacial acetic acid in yellow laminæ which melt at 219—220°. It exhibits all the properties of its lower homologue (Found : C = 77·6 ; H = 4·9. $C_{24}H_{18}O_4$ requires C = 77·8 ; H = 4·9 per cent.).

Reduction of ββ-*Di*-2-α-*naphthaquinonylbutane to* 5 : 9-*Dihydroxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen* (IV).

The reduction proceeds in an entirely analogous manner to that of the corresponding dimethyl compound. Similarly also, the reduction product is quite stable and readily purified.

5 : 9-*Dihydroxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen* crystallises from glacial acetic acid in colourless, thick, hexagonal plates containing a molecule of acetic acid of crystallisation, which is removed on exposure to the air (Found : acetic acid = 14·3. $C_{24}H_{20}O_3,C_2H_4O_2$ requires acetic acid = 14·4 per cent.). The resulting mauve-tinted powder darkens at 285° and melts at 299° (Found : C = 80·9 ; H = 5·7. $C_{24}H_{20}O_3$ requires C = 80·9 ; H = 5·6 per cent.). This dihydroxy-compound also crystallises from alcohol ; the solution displays a pale violet fluorescence.

5 : 9-*Diacetoxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen*, prepared in the usual manner, crystallises from glacial acetic acid in white, warty crystals, which melt at 221—223°. It is sparingly soluble in alcohol (Found : C = 76·3 ; H = 5·6. $C_{28}H_{24}O_5$ requires C = 76·4 ; H = 5·5 per cent.).

5 : 9-*Dibenzoyloxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen* is formed by heating the dihydroxy-compound with excess of benzoyl chloride for one minute only. The solution is poured into water containing a small amount of alkali, and vigorously stirred, and the product then separates as a white powder. It is sparingly soluble in glacial acetic acid, from which it crystallises well in colourless, short rods melting at 235—237°. It is very soluble in benzene and slightly soluble in alcohol (Found : C = 80·7 ; H = 5·2. $C_{38}H_{28}O_5$ requires C = 80·8 ; H = 5·0 per cent.).

5 : 9-*Dimethoxy*-7-*methyl*-7-*ethyl*-α-*dinaphthaxanthen*.—The addition of methyl sulphate (0·75 gram) to the pale apple-green solution (which rapidly turned dark bottle-green) of the dihydroxy-compound (1·1 grams) in 15 per cent. potassium hydroxide (5 c.c.) caused the deposition of a green precipitate, which turned brown and finally salmon-coloured. The mixture was warmed on the water-bath for a few minutes and separated. The product was crystallised from glacial acetic acid. At first there separated from the solution long,

sword-shaped, pale salmon crystals, then small, pure white, warty crystals. These melted at the same temperature. Repeated crystallisation gave long, ill-defined, colourless crystals, which melted at 228—230° (Found: C = 80·9; H = 6·3. $C_{26}H_{24}O_3$ *requires C = 81·2; H = 6·2 per cent.). The substance resembles* 5 : 9-dimethoxy-7 : 7-dimethyl-α-dinaphthaxanthen in solubility, but appears to be generally more soluble. It crystallises well from amyl alcohol, in which solvent it gives rise to a faint violet fluorescence.

Oxidation of 7 : 7-*Diethyl-α-dinaphthaxanthen* (*Anhydro*-γ-1 : 1-*dihydroxydinaphthylpentane*).

The experiment is conducted as given under the oxidation of the corresponding dimethyl and methyl ethyl compounds.

5 : 6 - *Diketo* - 7 : 7 - *diethyl* - 5 : 6 - *dihydro-α-dinaphthaxanthen* (I) crystallises from glacial acetic acid in large crystals, which are deep orange when prepared in the dark, but rapidly turn scarlet on the surface when exposed to light. The orange crystals melt at 224—227°. It also crystallises well from pyridine, acetone, or amyl alcohol, and is very soluble in alcohol or benzene (Found: C = 81·5; H = 5·4. $C_{25}H_{20}O_3$ requires *C* = 81·5; H = 5·4 per cent.).

A *mononitro*-derivative is obtained in the usual way. It crystallises readily from glacial acetic acid in salmon-red crystals, which melt at 282—284° (Found: N = 3·5. $C_{25}H_{19}O_5N$ requires N = 3·4 per cent.).

The *quinoxaline* crystallises as yellow rods from a solution containing equal volumes of alcohol and glacial acetic acid, or from pyridine diluted with water. It melts at 218—219°, and is very soluble in glacial acetic acid, and sparingly soluble in alcohol (Found: N = 6·3. $C_{31}H_{24}ON_2$ requires N = 6·4 per cent.).

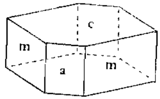
γγ-*Di*-2-α-*naphthaquinonylpentane* (II) crystallises from glacial acetic acid, or from pyridine, in yellow plates melting at 251°. Fuming nitric acid has no action upon it (Found: C = 78·2; H = 5·1. $C_{25}H_{20}O_4$ requires C = 78·1; H = 5·2 per cent.).

5 : 9-*Dihydroxy*-7 : 7-*diethyl-α-dinaphthaxanthen* (IV) is prepared from the preceding compound by reduction with zinc in glacial acetic acid. It crystallises from this acid in the form described below. The crystals become opaque at 90° and one molecule of acetic acid is lost. The pink-tinted powder shows signs of change at 250° and melts at 295° with decomposition (Found: acetic acid = 14·0. $C_{25}H_{22}O_3,C_2H_4O_2$ requires acetic acid = 14·0 per cent. Found: after removal of the acetic acid, C = 80·8; H = 5·8. $C_{25}H_{22}O_3$ requires C = 81·1; H = 5·9 per cent.).

Crystallographic measurement revealed that the crystals obtained

from acetic acid solution (containing one molecule of acetic acid), are monoclinic, $a : b = 0{\cdot}834$; $\beta = 104° \; 42'$. Forms: *a*{100}, *m*{110}, *c*{001}. The common habit is shown in Fig. 2, and is tabular parallel to *c*{001} and elongated along the *b*-axis. The crystals are poor; two, however, were found to be measurable, and the mean angular values obtained were:

FIG. 2.



	a{100}.	*m*{110}.	*c*{001}.
ϕ	89° 53½′ (+6½′)	*51° 7′	88° 16′ (+1° 44′)
ρ	90 21½ (−21½′)	89 53 (+7′)	*14 42

*Oxidation of 7-Methyl-7-*n*-propyl-α-dinaphthaxanthen (Anhydro-β-1 : 1-dihydroxydinaphthylpentane).*

The reaction is carried out as with the homologues. The viscid reaction mixture deposits the orange and the yellow oxidation products after scratching and long standing; their complete separation is difficult on account of similarity in solubility.

*5 : 6-Diketo-7-methyl-7-*n*-propyl-5 : 6-dihydro-α-dinaphthaxanthen* melts at 219—220°. It is much more soluble in glacial acetic acid than its homologues (Found: C = 81·5; H = 5·4. $C_{24}H_{20}O_3$ requires C = 81·5; H = 5·4 per cent.).

Attempts to nitrate this compound with fuming nitric acid in glacial acetic acid solution failed. The only product separated from the reaction mixture and identified was phthalic acid.

ββ-Di-2-α-naphthaquinonylpentane (II) crystallises from glacial acetic acid in thick, yellow laminæ melting at 203—204°. They contain acetic acid of crystallisation, which is removed at 130°. The resulting yellow powder gave C = 78·4; H = 5·4. $C_{25}H_{20}O_4$ requires C = 78·1; H = 5·2 per cent.

*Reduction of ββ-Di-2-α-naphthaquinonylpentane to 5 : 9-Dihydroxy-7-methyl-7-*n*-propyl-α-dinaphthaxanthen* (IV).

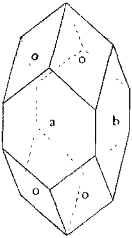
The reduction product, obtained in the usual way, does not contain acetic acid of crystallisation. It turns slightly brown at 275°, and melts with decomposition at 290° (Found: C = 80·9; H = 6·0. $C_{25}H_{22}O_3$ requires C = 81·1; H = 6·0 per cent.).

Crystallographic examination showed that the crystals are orthorhombic, $a : b : c = 0{\cdot}704 : 1 : 0{\cdot}793$. Forms: *b*{010}, *a*{100}, *o*{111}. The common habit (see Fig. 3) is pyramidal, with the pinacoids well developed, although the latter are curved and distorted. Three crystals were measured, and the mean angular values obtained for the form *o*{111} were as follow: ϕ *54° 51′; ρ *54° 1′.

A *dibenzoyl* derivative of 5 : 9-dihydroxy-7-methyl-7-*n*-propyl-α-

dinaphthaxanthen is obtained in the usual way. It crystallises in colourless rods from glacial acetic acid, and melts at 216—218°. It is almost insoluble in alcohol, very soluble in benzene, and appreciably soluble in carbon tetrachloride.

FIG. 3



Summary.

1. The condensation products of α-naphthol and ketones have been shown to be dialkyl substitution products of α-dinaphthaxanthen, in which the alkyl groups are attached to the carbon atom of the pyran ring.

The products examined are those derived from α-naphthol and the ketones, acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone respectively.

2. Oxidation of these 7 : 7-dialkyl-α-dinaphthaxanthens has given rise to two series of brightly coloured compounds, orange products containing an ortho-quinonoid grouping, and yellow products containing two para-quinonoid groupings.

3. The orange ortho-diketones are shown to be 5 : 6-diketo-7 : 7-dialkyl-5 : 6-dihydro-α-dinaphthaxanthens by the preparation therefrom of quinoxalines; and by reduction to hydroxy-compounds, and the formation from these of diacetyl derivatives. The production of a mononitro-derivative and the inability to prepare a dinitro-derivative are in support of the ortho-quinonoid structure, in which one naphthalene ring system is affected and the other unattacked. By further action of the nitrating agent, the orange compounds are oxidised to phthalic acid.

4. The yellow products have been proved to be di-2-α-naphthaquinonyldialkylmethanes by the facts that they do not form quinoxalines and are reducible to 5 : 9-dihydroxy-7 : 7-dialkyl-α-dinaphthaxanthens, the formation of which evidently follows the elimination of water from the intermediately formed tetrahydroxy-reduction products, since stable diacetyl, dibenzoyl, and dimethyl derivatives of the 5 : 9-dihydroxy-7 : 7-dialkyl-α-dinaphthaxanthens have been obtained.

5. The di-2-α-naphthaquinonyldialkylmethanes are unattacked by fuming nitric acid.

6. Their reduction products, 5 : 9-dihydroxy-7 : 7-dialkyl-α-dinaphthaxanthens, have been examined crystallographically.

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LXVI.—*Change of Properties of Substances on Drying.*

By HERBERT BRERETON BAKER.

IT was demonstrated in 1912 that the boiling points of the trioxide and tetroxide of nitrogen were raised by 44° and 47° respectively when they were allowed to stand for a long time in contact with phosphoric oxide (H. B. Baker and Muriel Baker, T., 1912, **101**, 2339). In the following year a number of other liquids were prepared in a state of high purity and sealed up in vessels containing purified phosphoric oxide. In many cases, direct contact of the liquids with the drying agent was avoided on account of possible chemical action, the drying being then dependent on the removal of water from the continually changing vapour. During the War, pressure of other work rendered it impossible to proceed with the experiments, so that when the work was resumed, last year, the substances had been drying for eight or nine years. In every case the boiling point, indicated by the formation of bubbles in the heated liquid, showed a large elevation, of 30° to 60°. Broken pieces of fused silica had been placed in each bulb so as to prevent ordinary superheating. The boiling, when it did take place, proceeded quite quietly; no sign of the violent ebullition which accompanies the breaking down of a superheated condition was observed. There was nothing, in the behaviour of the liquids, except the reading on the thermometers, which suggested anything abnormal in their boiling. In some cases, two thermometers were enclosed in the bulbs, one dipping in the liquid, and the other suspended about 3 cm. above its surface. The temperatures read on the latter were at most 2° above the normal boiling point of the liquid, and yet when the condensed liquid from the distillation was again heated it did not enter into a state of ebullition until the abnormally high temperature had been reached.

Experiments were tried with ten liquids of different types; the results are given in the following table:

	Period of drying. Years.	Original boiling point.	New boiling point.	Rise.
Bromine	8	63°	118°	55°
Mercury	9	358	420—425	62
Hexane	8½	68·4	82	14
Benzene	8½	80	106	26
Carbon disulphide	1+27	49·5	80	30
Carbon tetrachloride	9	78	above 112	34
Ethyl ether	9	35	83	48
Methyl alcohol	9	66	above 120	54
Ethyl alcohol	9	78·5	138	60
Propyl alcohol	9	95	134	39

The apparatus used consisted of a distilling flask of Jena-glass with two side tubes. To one of these tubes was sealed the side piece of another distilling flask, whilst the other was drawn out to a long tube about 2 mm. in diameter. The necks of the distilling flasks were lengthened by fusing on tubes of similar diameter, which were bent down at the top to form convenient receptacles for the phosphoric oxide. The apparatus was cleaned by allowing a mixture of chromic and concentrated nitric acids to stand in it for some hours. It was washed with distilled water and dried by heating, nearly to redness, while a current of air, dried by sulphuric acid and phosphoric oxide, was drawn through every part. Fragments of fused quartz, previously ignited, were placed at the bottom of each flask. After the introduction of the liquids, the openings were sealed and left for the period of drying. In the cases of liquids where no chemical action on the pentoxide was to be feared, such as benzene, hexane, or bromine, one plug of the drying agent was placed with the liquid in one of the distilling flasks. In other cases, the drying was performed only on the vapour. In no case, even with the alcohols, was any increase of pressure noticed when the narrow tube was opened. To determine the boiling point, the tip of the long tube was dipped under previously boiled mercury and the depth of the open tube was noted. The liquid was distilled by heating the flask containing it in an oil-bath, the other flask being cooled in water or in ice. When sufficient of the liquid had been collected in the previously empty flask, the latter was heated in the oil-bath while the other was cooled. The heating of the oil-bath was conducted very slowly so as to allow of the liquid fully attaining the temperature of the oil. When the temperature was approaching the boiling point, the heating was slowed down still more, so that half an hour was occupied in raising the temperature through 5°.

Details of some of the experiments are given below.

Bromine.—This had been purified for atomic weight purposes by Stas's method. It had been drying over phosphoric oxide for a year, before its use for these experiments.

Mercury was purified by shaking with mercurous nitrate. It was then distilled in a vacuum, shaken for a long time in air, filtered, and re-distilled. The boiling point was determined by heating in a short, wide silica tube closed at the bottom, and converted into an electric furnace by a coil of nickel-chrome wire, covered by a thick layer of asbestos cloth. The temperature was determined by the simultaneous use of a platinum-rhodium couple, and by a Jena-glass thermometer filled with nitrogen. The mercury was maintained at 360° for half an hour. Not only was there no boiling, but only the faintest trace of sublimate appeared above the surface of the liquid. Bubbles of vapour first escaped at 420°, but active ebullition was only apparent at 425°.

Hexane.—This was obtained from Kahlbaum. It was dried by shaking with phosphoric oxide for some days, and distilled into the drying apparatus. In the determination of the boiling point of this liquid, the temperature of 82° was reached before any bubbles appeared. The tube connecting the two flasks was accidentally broken, and the liquid was left exposed to the air over-night. Next morning it was expected that the boiling point would have fallen, but the boiling point was 81°. Some of the liquid was transferred to a new distilling flask which had not been specially dried. The temperature of ebullition, as measured by a thermometer in the liquid, was still 81°, whilst that in the vapour was 68·4°, the original boiling point.

Benzene, obtained from Kahlbaum, had a boiling point of 79·5°. It was dried by phosphoric oxide and distilled into the apparatus. The apparatus was provided with two thermometers. The temperature of the oil-bath was raised very slowly. When it had reached 105°, there was manifest evaporation, and liquid could be seen dropping from the upper thermometer, which gave a reading constantly of 80°. On one occasion these drops, falling on the surface of the hot liquid below, formed a globule about 12 mm. in diameter and 5 mm. deep, which persisted for more than a minute. When it coalesced with the rest of the liquid, it did so without any disturbance, and there was no perceptible increase in pressure in the apparatus. The liquid boiled at 106° quite steadily. Some of the liquid was distilled from the apparatus into a distilling flask and left for a day exposed to moist air. Its boiling point was found to be 105°. It was then shaken with water, and it was found that the water could be boiled through the layer of benzene, only slow evaporation of the latter taking place. In time, however, the liquid regains its normal boiling point. The original apparatus, above described, was allowed to cool and to draw in air dried by sulphuric acid and phosphoric oxide. It was then sealed up, but on testing a month later, the boiling point was found to be 81°.

The temperature of ebullition of benzene was found to be 106° in three different pieces of apparatus, sealed up within a few days of each other (March, 1913). In two others, dried for about two months longer, the boiling point was found to be 118°. The boiling in the latter two tubes was not as steady as in the former, being more violent, and suggesting some degree of ordinary superheating. (The boiling point of the benzene in the experiment shown at the meeting of the Chemical Society was 109°.)

Carbon Disulphide.—A bottle of this substance was found in the laboratory which had been purified by J. W. Rodger in 1894. The bottle contained phosphoric oxide, the stopper being covered with oiled silk. This liquid was distilled into a tube, dried by pentoxide, the boiling point being 49·5°. The tube was sealed up for a year. On testing this with a very low barometric pressure of 730 mm., the first sign of vaporisation was found at 60°. The vapour was seen to condense on the tube, and the liquid ran down in oily drops which coalesced with the main body of the liquid without any sudden production of vapour. The first bubble was seen at 80°; at 81°, ebullition was general throughout the liquid.

Carbon tetrachloride, obtained from Kahlbaum, was saturated with chlorine, boiled to drive off the gas, and allowed to stand in contact with solid sodium hydroxide. It was distilled into a bottle containing phosphoric oxide, and distilled into the drying apparatus a month later. This was tested early in 1914, but the record of the temperature at which it had been sealed up was lost. It was therefore not known when it would be safe to break the tip of the long tube under the dried mercury. This was done prematurely, when the temperature was 100°, and the mercury rose in the long tube to a height of 80 mm., so that under the diminished pressure of 670 mm. the carbon tetrachloride did not boil. At 112°, ebullition commenced.

Ethyl ether, obtained from Kahlbaum, was not left in contact with phosphoric oxide. Liquid tended to collect in the part of the apparatus containing the drying agent, but was distilled off without opening the apparatus. Boiling began at 83°. Some of the liquid was distilled into another distilling flask, dried only by heating and drawing dried air through it. This boiled at 47°, the thermometer in the vapour registering 35°. Next day the liquid, exposed to the comparatively moist air, boiled at 36°. In this case the recovery of the normal state was much more rapid than in the former instances.

The three alcohols were obtained from Kahlbaum and dried without contact of the liquid with phosphoric oxide. The distilled liquids recovered their normal boiling points when exposed for a very short time to ordinary air.

Some preliminary experiments have been done on the measurements of the vapour pressures of the dried liquids, using a dried barometer tube of mercury surrounded by a water-jacket. Dried ether, on being admitted to the tube, gave at 20° a vapour pressure of 374 mm. instead of 442, as measured by Ramsay and Young (*Proc. Roy. Soc.*, 1886, **40**, 381).

In every case the liquid distilled from the dried apparatus was tested for the presence of phosphoric acid, and no trace could be detected. The phosphoric oxide was obtained by slow distillation of the purest pentoxide obtainable commercially, in a current of dried air. The distillation proceeds best at a temperature of between 250° and 300°, and if this temperature is not exceeded, a tube can be used many times. An electric furnace is most convenient for the purpose. When conducted properly, the pentoxide is obtained in two forms, in feathery crystals and in a fine, white powder. Its freedom from lower oxides of phosphorus is proved by its producing no precipitate with mercuric chloride, and no darkening with ammoniacal silver nitrate. Only about one-tenth of the pentoxide used is obtained as a pure product.

The hypothesis suggested in the former paper was that in liquids there is normally a balance between associated and dissociated molecules, and that, as has been shown with many vapours, the absence of water vapour tends to prevent dissociation. The boiling point of the dried liquid, consisting mainly of associated molecules, is, as would be expected, much higher than that of the normal liquid.

It was thought that evidence for or against this view might be obtained by measuring the surface tension of the liquids. The procedure of Ramsay and Shields (T., 1893, **63**, 1089) was followed almost exactly, greater precautions being taken in drying the tubes and the capillaries. The diameter of the capillaries was measured for me by Miss M. Carlton, using a very fine reading microscope in the Astrophysics Department of the College, which reads directly to 0·01 mm. Those which were not truly cylindrical were rejected, and a number of pairs were obtained the measurements of which not only coincided, but which gave identical results when tested with benzene. The capillaries were attached to their sinkers, washed with nitric and chromic acids and distilled water, and heated nearly to softening point while a current of air was drawn through them; they were then allowed to cool in a desiccator over phosphoric oxide. As results were desired as soon as possible, those liquids were chosen which could be left in contact with phosphoric oxide without the possibility of chemical action or solvent power on the drying agent. The liquids were as dry as could be obtained at the

time, one of each pair containing phosphoric oxide, and the other not. The progress of the drying was rendered visible by the greater rise in the capillary tube in the liquid containing the pentoxide. The actual measurements were made a year after the tubes had been sealed. Great difficulty was experienced in locating with the reading microscope the precise point at which the capillary tube entered the liquid in the wider tube, the latter being of the width recommended by Ramsay and Shields. As, however, the results were comparative, this was not of paramount importance.

Bromine gave in a tube of 0·085 mm. radius a capillary rise 0·975 mm. higher in the dry tube than in the undried liquid at 7°, and 0·5 mm. higher at 32°. Assuming that the heights were correctly measured, the factor by which the molecular weight must he multiplied would be 1·34 for the undried liquid and 1·99 for the dried liquid. It may here be recalled that the vapour density of bromine just above its boiling point is greater than normal, 82 instead of 80 (Jahn, *Ber.*, 1882, **15**, 1238). Benzene gave in a tube of 0·111 mm. radius a capillary rise 13·73 mm. higher in the dry liquid than in the undried at 16·5°, and 15·65 mm. higher at 35°. Making the same assumption as before, the multiple of the molecular weight for dried benzene was 3·39, whilst that for the undried liquid was 1·28.

For hexane, the multiple of the molecular weight found for the dry liquid was 3·16, that for the undried liquid 0·92. It may be noted that Ramsay and Shields gave 0·93 for *n*-octane, and as there is no possibility of dissociation for these liquids, his so-called normal liquids were to some extent associated, and the true value of k ought to be at least 2·28 instead of 2·121.

With nitrogen tetroxide the diameter of the capillaries in the two tubes was not the same. The result gave as the multiple for the molecular weight 3·10 for the liquid containing the drying agent and 3·00 for that of the liquid alone. This close agreement is probably to be accounted for by the fact that the liquid in both tubes was distilled from a specimen which had been drying over pentoxide for ten years. It was thought that there would have been sufficient moisture left in the tube which was being filled to convert it into an undried liquid, but this apparently was not the case.

Density.—It was thought that such a profound change as seemed to take place in the liquids on drying would be shown also by a change in density. The following liquids were filled into dilatometers containing phosphoric oxide: benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, and nitrogen trioxide. After standing for a year, the volumes are unchanged, although a change of 1 part in 10,000 would have been easily recognisable.

Melting Point.—A tube containing sulphur which had been purified for atomic weight purposes was set up for me in 1913 by Mr. A. H. Bennett. Its melting point, determined at the time, on a thermometer enclosed in the tube, was 112·5°. The same reading was obtained in 1914. Now, however, the melting point is 117·5°.

Dr. Smits of Amsterdam, with whom I have been in correspondence, points out that this is a confirmation of his recent theory of allotropy.

The rise in the melting point of iodine, also purified for atomic weight purposes, is from 114° in 1913 to 116° in 1922.

Experiments are in progress for determining the specific heat of the dried liquids and the densities of their vapours.

Summary.

The points of ebullition of ten liquids which have been dried by the agency of phosphoric oxide for extended periods show a very considerable rise.

The hypothesis that this is caused by increased molecular complexity receives support from preliminary determinations of the surface tensions of the dried liquids.

The melting points of sulphur and iodine show rises of 5·5° and 2° respectively after nine years' drying.

The densities of seven liquids show no change after drying for a year in contact with phosphoric oxide.

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SOUTH KENSINGTON, S.W.7. [*Received, March 16th*, 1922.]

LXVII.—*Piperitone. Part II. Benzylidene*-dl-*piperitone.*

By JOHN READ and HENRY GEORGE SMITH.

IN a recent preliminary paper (T., 1921, **119**, 779) dealing with the chemistry of the eucalyptus ketone, piperitone, we described the preparation of benzylidene-*dl*-piperitone and indicated the importance of this very distinctive derivative in differentiating piperitone from closely related ketones. At the same time, we suggested that the remarkable ease with which the derivative is formed was likely to prove of interest in connexion with the question of the constitution of piperitone. For these reasons it was thought advisable to examine more fully the physical and chemical characteristics of benzylidene-*dl*-piperitone and to carry out supplementary experiments bearing on its formation. Some of the results of these investigations are recorded in this communication. In particular,

the dimorphism of benzylidene-*dl*-piperitone, of which an indication was given in our first paper, bas proved to possess bighly characteristic and interesting features.

Among the work not fully described, may be mentioned certain attempts to prepare definite benzylidene or dibenzylidene derivatives of carvone; these experiments were carried out with the object of gathering further evidence regarding the constitutional peculiarities whicb allow of this condensation. Our observations confirmed Wallach's statement (*Annalen*, 1899, **305**, 274) that carvone condenses readily with benzaldehyde in alkaline solution to give ill-defined products. By using alcoholic sodium ethoxide as a condensing agent, in the way described for piperitone (*loc. cit.*, p. 785), it was found that carvone reacted with great ease with two molecular proportions of benzaldehyde; the product, however, could only be obtained in the form of a yellow, vitreous mass. When one molecular proportion of benzaldehyde and one-fifth tbe preceding amount of sodium were used, the product was a pale yellow oil of indefinite boiling point, the bulk of which distilled below 240°/20 mm. At this point in the investigation the recent paper by Müller (*Ber.*, 1921, **54**, [*B*], 1471) came under our notice, describing the production of a solid and a liquid monobenzylidenecarvone by carefully controlled alkaline condensation. Further work in this direction was accordingly abandoned. Incidentally, we may point out that the substance melting at 233—234° obtained by Müller (*loc. cit.*, p. 1480) in small yield by the action of phenylcarbimide on benzylidenedihydrocarveol and on α- and β-benzylidenecarvones is probably not a phenylurethane, as stated. The high melting point of this substance, which apparently was not analysed, suggests that it was carbanilide, and thus the presumed identity of the reduced α- and β-benzylideneearvones with benzylidenedihydrocarveol cannot be accepted as established.

EXPERIMENTAL.

Dimorphic Forms of Benzylidene-dl-*piperitone*.

In the original crystallisations of benzylidene-*dl*-piperitone (*loc. cit.*, p. 787) two forms of crystals were observed; these were characterised by distinctive habits, one form being prismatic and the other tabular. As a result of goniometric measurements, the crystals of prismatic habit (now named the α-form) were assigned to the monoclinic system, but owing to incomplete development of the observed crystals the axial ratios could not be determined in full. In an attempt to secure more perfect crystals of this kind by recrystallisation from etbyl-alcoholic solution, a striking transformation occurred and the whole of the material separated as

crystals of tabular habit (the β-form). Further recrystallisations confirmed this result; it appeared impossible, in fact, to reproduce the effect of the original crystallisation. Ultimately, however, by inoculating a supersaturated alcoholic solution of the substance with a portion of a powdered crystal of prismatic habit, a homogeneous separation of crystals of this type was obtained. Similarly inoculation with material from a crystal of tabular habit resulted in a separation consisting entirely of crystals of the second type. In brief, by suitable inoculation, it was found possible to induce benzylidene-*dl*-piperitone to crystallise wholly in either of the forms mentioned; perfectly homogeneous separations of the α- and β-form being thus obtainable at will. Crystallisation was effected in all cases at the ordinary temperature, the solvent being either methyl alcohol or ethyl alcohol. The tendency of the substance to form supersaturated solutions has already been mentioned; a perfectly sterile alcoholic solution of this kind may be kept indefinitely in a closed vessel without crystallisation occurring at all.

*α-Benzylidene-*dl*-piperitone* forms pale yellow prisms, often exceeding 1 cm. in length and exhibiting high transparency and lustre. The powdered crystals are almost colourless. The crystals appear to be quite stable when kept in the dark, but after several months' exposure to diffused light they gradually lose their lustre and become gummy. This effect is greatly accelerated in bright sunlight; after a few minutes' exposure a distinct change is noticeable; after an hour or so, opalescence begins to radiate from numerous centres; and eventually, after several hours, this appearanee becomes general, whilst the faces assume a vitreous aspect and the crystals cohere. If the exposure has been made in a closed glass tube, a distinct odour of benzaldehyde becomes evident at this stage.

Crystals from five different preparations melted in each instance over the range 59—61°, when powdered and heated in a capillary tube in the usual way. No preliminary sintering was observed, and after resolidification the specimens melted with somewhat greater precision, the mean range being 59—60°.

These crystals show a strongly developed tendency to assume the simple forms already illustrated (*loc. cit.*, p. 786), and hour-glass structure is a very typical feature. It was only after numerous attempts, extending over several months, that crystals were obtained of suitable development to permit of full crystallographic characterisation. The appended supplementary report was kindly supplied by Miss Marie Bentivoglio, B.Sc., of the Department of Geology, University of Sydney:

"Recently obtained crops of crystals of α-benzylidene-*dl*-piperitone have yielded individuals exhibiting two extra pyramidal forms: consequently, it has now been possible to determine the complete axial ratios. These forms (Fig. 1) are $d(\bar{1}11)$, a long narrow face, and $e(\bar{1}21)$, a small form only observed on two crystals. The prismatic crystal habit remains unaltered.

"*Axial ratios.*—$a : b : c = 0{\cdot}9321$ * $: 1 : 0{\cdot}3899$. $\beta = 72°\ 36'$.

Form.	No. of measurements.	Limits. ϕ	Limits. ρ	Observed. ϕ	Observed. ρ
$d(\bar{1}11)$	6	17° 11′—17° 45′	22° 22′—21° 52′	17° 28′	22° 14′
$e(\bar{1}21)$	2	8° 58′— 9° 15′	38° 00′—38° 23′	9° 07′	38° 12′

"The calculated ϕ and ρ for $e(\bar{1}21)$ are, respectively, 9° 06′ and 38° 18′."

FIG. 1.

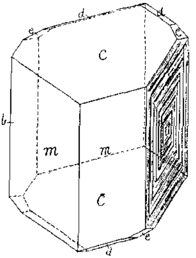
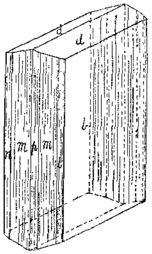


FIG. 2.



β-*Benzylidene*-dl-*piperitone* forms lustrous, transparent crystals having a pronounced yellow colour and attaining a length of 2 or 3 cm. The yellow colour is equally evident in the powdered crystals; indeed, powdered specimens of the α- and β-forms of this substance may easily be differentiated by reference to their colour alone. The crystals are quite stable in diffused daylight, and even when exposed to bright sunlight no alteration is apparent until the lapse of about a fortnight. On prolonged exposure, however, the crystals gradually become gummy, although no opalescence is developed. As with the α-form, the change appears to be accompanied by the production of minute amounts of benzaldehyde.

It may be remarked in this place that the last-named observation cannot be interpreted as an indication of any pronounced tendency on the part of this derivative to revert to benzaldehyde and piperitone under ordinary chemical influences. Attempts to hydrolyse

* The value of *a* has been corrected from 0·9331 to 0·9321.

it with hot aqueous acid and alkali showed that benzylidene-*dl*-piperitone is practically unaffected by these reagents. Thus, up to the present, it has not proved possible to utilise this readily accessible derivative for the regeneration of pure *dl*-piperitone : such a process would be very desirable in view of certain objections associated with the semicarbazone process, to which attention will be directed in a later communication.

Crystals from five different preparations of β-benzylidene-*dl*-piperitone melted in each instance over the range 63—64°, with a slight preliminary sintering at about 61°. After resolidification in the capillary tube, each of these specimens melted at 59—60°.

Crystals of the β-form invariably exhibit striations, but the hour-glass structure, characteristic of the α-form, is not evident. A goniometric examination of these crystals was also made by Miss Bentivoglio, to whom we are indebted for the following particulars :

"The crystals of β-benzylidene-*dl*-piperitone are transparent and light yellow in colour. Although varying much in size, they preserve a perfect tabular habit, the brachypinacoid being the largest form present (Fig. 2). The prism zone is well developed and contains the form *b*(010) having a smooth surface, and the forms *l*(250), *n*(470), *m*(110), and *p*(310), all of which are strongly striated, so that very accurate readings could not be obtained. The dome *d*(013) is invariably present and has smooth faces. A well-marked cleavage was observed parallel to *b*(010).

"*Crystal system.*—Rhombic, normal.

"*Axial ratios.*—$a : b : c = 0{\cdot}4841 : 1 : 0{\cdot}9334$.

Angle.	No. of measurements.	Limits.	Observed.	Calculated.
bl = 010 : 250	10	39° 15′—40° 14′	39° 51′	39° 34′
bn = 010 : 470	12	49° 14′—49° 54′	49° 34′	49° 44′
bm = 010 : 110	19	63° 45′—64° 23′	64° 10′	64° 10′
bp = 010 : 310	27	80° 39′—81° 19′	81° 02′	80° 50′
bd = 010 : 013	24	72° 17′—72° 59′	72° 43′	72° 43′
dd = 013 : 013	11	34° 09′—34° 51′	34° 34′	34° 34′

"It would appear, therefore, that the two forms of crystals are in no way correlated. The prismatic crystals are monoclinic; the tabular ones are rhombic. This difference is also observed in optical properties. The tabular crystals possess rectangular extinction directions, parallel to the two edges of the crystal; in the monoclinic crystals (the ortho-zone being usually absent), inclined extinction was observed. Moreover, a biaxial interference figure was obtained for the tabular crystals, symmetrical about the centre of the microscope field."

The fact that the dimorphic substance, benzylidene-*dl*-piperitone,

tends to separate from alcoholic solutions at the ordinary temperature in the β-form, taken in conjunction with the comparatively sluggish response of this form to the influence of sunlight, might perhaps be accepted as an indication that the β-form is stable and the α-form labile at the ordinary temperature. If this supposition were correct, the dimorphism would obviously be monotropic, in view of the higher melting point of the β-form. Further experiments, however, demonstrated that the α-form is the stable modification at the ordinary temperature. When a saturated mother-liquor in contact with rhombic crystals is seeded with monoclinic material, the rhombic crystals are rapidly etched and dissolved, while monoclinic crystals develop at their expense, until, after the lapse of one or two days, all the original rhombic crystals have disappeared. The particularly well-developed monoclinic crystals described above were obtained in this way. It follows, therefore, that the α-form is the less soluble and the more stable at the ordinary temperature; further, since the β-form has the higher melting point, the dimorphism is enantiotropic. No accurate determinations of solubility or density have yet been made, but the behaviour of the two forms when raised gradually to the region of the melting point suggests that the transition temperature is situated not far below that region. It may be added that either modification may be preserved indefinitely when allowed to remain in contact with its saturated mother-liquor in a closed vessel.

When molten benzylidene-*dl*-piperitone is allowed to solidify, it invariably assumes the α-form. This fact accounts for the production of the original monoclinic crystals, the solution having been seeded with material obtained in this way. Probably, the rather unusual relationships which have been observed between these dimorphic modifications may be explained by assuming that their difference of stability is much less pronounced than is customary in such cases. Thus, the molten material undergoes a preliminary solidification to the α-form, which, although labile at the melting point, is sufficiently stable to persist until the temperature has fallen below the transition temperature. Similarly, solutions crystallising at the ordinary temperature yield a preliminary deposit of the labile β-form, which, however, is so stable at this temperature that it exhibits no apparent tendency to undergo transformation into the less soluble and theoretically more stable α-form, unless it is brought into contact with that form.

Benzylidene-*dl*-piperitone thus appears to present one of the best-defined cases of enantiotropic dimorphism yet recorded in organic chemistry, the ease with which each form is procurable in a state of freedom from the other being especially remarkable.

The only solvents yet applied in studying the relationships concerned are methyl alcohol and ethyl alcohol, and no appreciable difference has been observed in their effects. Cold alcoholic solutions of benzylidene-*dl*-piperitone exhibit a pale yellow colour, which deepens appreciably on heating and pales to the original tint as the solution cools.

When the substance, after being heated considerably above the melting point, until it becomes quite mobile, is poured into ice-water it forms a pale yellow, semi-fluid, plastic mass, which after standing for about ten minutes becomes crystalline.

Since benzylidene-*dl*-piperitone is an externally compensated substance, it seemed desirable to ascertain whether it is capable of optical resolution by spontaneous separation of its enantiomers in distinct crystals, according to the first method of Pasteur. From the above description it is apparent that neither of the dimorphic modifications exhibits asymmetry of form, and in conformity with this observation large individual crystals of both types yielded optically inactive solutions when dissolved in alcohol.

In view of the interesting results now recorded, it seems likely that the colour changes noted in the case of benzylidene-*dl*-piperitoneoxime (*loc. cit.*, p. 788) may also be ascribed to the occurrence of polymorphic forms. We propose to undertake further investigations in this field of work.

*The Addition of Hydrogen Bromide to Benzylidene-*dl*-piperitone.*

The ready manner in which such substances as benzylidenementhone and benzylidenecamphor combine with hydrogen bromide rendered it of interest to apply a similar reaction to the benzylidene derivative of *dl*-piperitone. The derivative was dissolved in eight times its weight of a 32 per cent. solution of hydrogen bromide in glacial acetic acid. The resulting dark red solution deposited brick red crystals, from which, after a few days, the supernatant liquid was decanted. The crystals dissolved readily in alcohol, acetone, or ether, forming colourless solutions which deposited the original benzylidene derivative when allowed to evaporate at the ordinary temperature. When triturated with cold benzene, in which they were insoluble, the crystals gave a bright yellow, crystalline mass, with apparent loss of hydrogen bromide. The yellow substance, which melted and sublimed at 91—95°, was stable in dry air, but in contact with water, alcohol, acetone, etc., it reverted to the benzylidene derivative, with the liberation of one molecular proportion of hydrogen bromide (Found: HBr = 22·7. $C_{17}H_{20}O$ + HBr requires HBr = 25·2 per cent.).

Very similar colour changes were observed when benzylidene-*dl*-

piperitone was dissolved in a mixture of concentrated sulphuric acid and acetic anhydride. The original deep orange solution changed to red, and soon yielded a thick, yellow, crystalline mass, which, after the lapse of an hour, changed to a dark brown liquid.

These observations recall the interesting work of Vorländer and his pupils on the addition of acids to certain unsaturated ketones (*Ber.*, **1904**, **37**, 1644; *Annalen*, 1906, **345**, 155).

The Reduction of Benzylidene-dl-*piperitone.*

For reasons which will be indicated later, it was considered of importance to investigate the reduction of benzylidene-*dl*-piperitone. The derivative (25 grams) was accordingly dissolved in absolute alcohol (250 c.c.) and reduced vigorously in hot solution with sodium (30 grams). From the clear, pale yellow solution which resulted was isolated, by following the usual procedure, a faintly yellow and rather viscous oil (15·5 grams); this product boiled at 197—210°/18 mm. and showed no tendency to crystallise, even after keeping for several months. When dissolved in chloroform, it decolorised bromine immediately, and from the analysis given below it evidently possessed the composition of a *benzyl*-p-*menthenol*, $C_{17}H_{24}O$. Attempts to effect a more vigorous direct reduction of the benzylidene derivative resulted in the production of resinous matter.

When heated on the water-bath with phenylcarbimide, the reduction product reacted without difficulty to form a *phenylurethane*; this compound crystallised readily from warm benzene in lustrous, feathery needles, melting at 140—141° (Found: C = 79·31; H = 8·03. $C_{24}H_{29}O_2N$ requires C = 79·28; H = 8·05 per cent.). At the same time, an appreciable amount of carbanilide was produced, the identity of which was established by analysis and melting point (241°, corr.). Incidentally, hot nitrobenzene was found to be an excellent solvent for this substance.

Further Observations on the Condensation of Piperitone with Benzaldehyde.

A specimen of *l*-piperitone, having $[\alpha]_D^{20} = -45·2°$, reacted readily with benzaldehyde, in the manner described for *dl*-piperitone (*loc. cit.*, p. 785), to yield a dark reddish-brown liquid product. By inoculation with α-benzylidene-*dl*-piperitone, it proved possible to isolate crystalline material from this crude, undistilled product. The resulting crystals consisted of α-benzylidene-*dl*-piperitone, and not only these crystals but also the oily mother-liquor failed to exhibit optical activity in benzene solution. It is thus apparent that complete racemisation occurs during the reaction, since the

method of purification adopted in this case precludes the possibility of subsequent racemisation.

The great ease with which this condensation occurs in the presence of a little sodium ethoxide rendered it of interest to investigate the effect of hydrogen chloride as a condensing agent in the reaction concerned. This method of condensation, which was shown by Wallach (*Annalen*, 1899, **305**, 261) to give excellent results in the case of menthone, yielded, however, only about 20 per cent. of the quantity of benzylidene-*dl*-piperitone obtained in the alkaline condensation.

We acknowledge our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of these researches, which are being continued.

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LXVIII.—*Piperitone. Part III. The Oximes of* dl-*Piperitone.*

By JOHN READ, HENRY GEORGE SMITH, and MARIE BENTIVOGLIO.

IN the original account of the characterisation of piperitone (T., 1921, **119**, 779), attention was directed particularly to four crystalline derivatives of this ketone, namely, *dl*-piperitone-hydroxylamino-oxime, *dl*-piperitoneoxime, *dl*-piperitonesemicarbazone, and benzylidene-*dl*-piperitone. The results of a more detailed examination of the last-named substance were described in a recent communication (this vol., p. 574). Concurrently with the latter investigation, the reactions involved in the formation of the remaining three derivatives were accorded further study; this led, in each case, to observations of considerable interest. One section of the work in question forms the subject of the present paper.

The yields of oxime obtained by the original method (*loc. cit.*, p. 784) were unsatisfactory, and the preparations often contained appreciable quantities of the hydroxylamino-oxime. Thus, in view of the importance, in a study of the chemistry of piperitone, of obtaining ready access to *dl*-piperitoneoxime, it became necessary to investigate modified methods of producing this derivative; the process described below is the best of about thirty such modifications which were examined, some of which, it may be remarked, led to almost quantitative yields of hydroxylamino-oxime. The majority

of the preparations of oxime obtained in the course of this work, after one or two recrystallisations from alcohol, melted at 118—119°; it seemed likely, therefore, that the original preparation (*loc. cit.*, p. 784), which, like a number of subsequent preparations, melted in the vicinity of 110°, contained a small amount of an isomeric substance. This proved to be the case, and eventually a more soluble oxime (now named the β-oxime) was isolated, melting at 88—89°.

The oximes of *dl*-piperitone possess an unusual capacity for crystallisation, and accordingly we have been able to record full crystallographic data for both forms. It may conveniently be stated in this place that, in general, the exceptional beauty of the crystalline derivatives of this ketone suggests a comparison, in this respect, between piperitone and camphor. *dl*-Piperitone-α-oxime forms magnificent, triclinic prisms, and gives rise to well-defined derivatives, including a characteristic hydrochloride crystallising in the rhombic system; this derivative reverts to its components in presence of water. The α-oxime reacts with *p*-nitrobenzoyl chloride and similar acid chlorides with great ease; the resulting derivatives, when submitted to the action of hydrogen chloride in benzene solution, appear to yield unstable additive products, which readily undergo hydrolysis, with loss of the acyl radicle. *dl*-Piperitone-β-oxime forms well-developed monoclinic prisms. No distinctive derivative of the β-oxime has yet been prepared, and the ease with which it is converted into derivatives of the α-oxime suggests that these two oximes are *syn*- and *anti*-forms, the β-oxime being the labile isomeride. The stability of the β-form is worthy of particular remark. No direct interconversion of the free oximes has yet been observed; in fact, each form may be regenerated unchanged from its solutions in mineral acids. It may thus be suggested that, like the dimorphic modifications of benzylidene-*dl*-piperitone, these stereoisomeric forms of *dl*-piperitoneoxime exhibit less difference in stability than is customary in similar cases.

In spite of the ease with which well-developed crystals may be obtained, neither of the oximes of *dl*-piperitone has been observed to undergo spontaneous optical resolution by the method of crystallisation. The preparation of such optically active forms by other methods, which are receiving attention, should enhance the general interest of the observations now recorded, notably in their relation to the chemistry of similarly constituted natural ketones the oximes of which appear, in general, not to exist in *syn*- and *anti*-forms.

During the course of the investigations of which the first section is now described, a copy of the interesting paper by Simonsen (T., 1921, **119**, 1644) on the essential oil of the Indian grass, *Andropogon*

Jwarancusa, became available through the courtesy of the author. That the ketonic constituent of this oil is *d*-piperitone, as suggested by Simonsen, is borne out by the indubitable identity of our Australian benzylidene-*dl*-piperitone and *dl*-piperitone-α-oxime, respectively, with the corresponding Indian products described by Simonsen. In the case of the oxime, full crystallographic correspondence was established by direct goniometric comparison, as described below. At a later stage in these investigations, we hope to discuss other observations associated with this highly interesting result and with the closely related question of the identity of piperitone (compare Simonsen, *loc. cit.*).

The natural production of piperitone in dextro- and lævo-gyrate modifications recalls the similar two-fold occurrence of a number of important related ketones, including carvone, menthone, fenchone, and camphor. As already indicated (*loc. cit.*, p. 780), the occurrence of piperitone has been established in the leaf-oils of numerous species of the genus *Eucalyptus*, but up to the present the only optically active form isolated from these sources has been lævorotatory. The low optical rotation of the specimens obtained in the majority of instances (Baker and Smith, " A Research on the Eucalypts," 2nd. ed., Sydney, 1920, 390) must probably be attributed to the ease with which the optically active ketone racemises during the process of isolation. The fact that piperitone has almost invariably been found in these oils in association with lævorotatory α-phellandrene (*loc. cit.*, p. 781) might perhaps be cited as an indication of the probable sense of rotation of the ketone in the original oils; on the other hand, it may be recalled that different species of this genus produce *d*- and *l*-pinene, respectively, whilst the *d*- and *l*-forms of α-terpineol have also been noted (Baker and Smith, *op. cit.*, 407, 369). In the exceptional instance of the oil of *E. apiculata*, which contains *d*-pinene but apparently no phellandrene, it has been shown that piperitone has a lævorotation somewhat smaller than in the oil of *E. dives*, which has a high content of *l*-α-phellandrene. Altogether, piperitone is known to occur in twenty-three species of *Eucalyptus*,* and it is only in the two species just mentioned that the character of its rotation in the natural oil

* Namely, *E. amygdalina*, ditto var. *nitida*, *E. Andrewsi*, *E. apiculata*, *E. Australiana*, *E. campanulata*, *E. coccifera*, *E. coriacea*, *E. Delegatensis*, *E. dives*, *E. fraxinoides*, *E. linearis*, *E. Luehmanniana*, *E. oreades*, *E. phellandra*, *E. piperita*, *E. radiata*, *E. regnans*, *E. Risdoni*, *E. Sieberiana*, *E. stellulata*, *E. tæniola*, *E. virgata*, and *E. vitrea*. It is remarkable that all these species have " white " timbers and occur in the south-eastern portion of Australia; so far, piperitone has not been found in any of the red- or brown-timbered species which are extensively distributed over the remaining portion of Australia.

has been established with any precision. Thus, the information at present available suggests that *l*-piperitone is always the predominant form, but that further work is necessary in order to ascertain definitely whether *d*-piperitone, or *dl*-piperitone, occurs in the essential oils of this genus.

Experimental.

The Preparation of dl-*Piperitoneoximes.*

In the original method described for the preparation of *dl*-piperitoneoxime (T., 1921, **119**, 784), the ketone (10 grams) was heated in aqueous alcoholic solution with one molecular proportion of hydroxylamine hydrochloride and an excess of potassium hydroxide. The resulting oxime, after crystallisation from light petroleum, melted at 110—111°. The yield was low, and further investigation showed that it was depressed by increasing the amount of alkali, most of the ketone then remaining unchanged. When kept at the ordinary temperature for a fortnight, the same reagents gave a small yield (3·6 grams) of the hydroxylamino-oxime, and no oxime. On the other hand, by adding somewhat less than one equivalent of potassium hydroxide and heating under reflux for two hours the yield of oxime was augmented, 10 grams of ketone furnishing 4·2 grams, which melted at 107—109° after one recrystallisation from light petroleum and ether. Replacement of the potassium hydroxide by sodium hydrogen carbonate in the last method led to very unsatisfactory results; in one such instance the aqueous alcoholic solution was heated under reflux for two hours, whilst in another it was warmed to about 40° at intervals extending over several days.

In other experiments, water was used in place of aqueous alcohol. An aqueous solution of hydroxylamine hydrochloride failed to react with piperitone, even when shaken with it for several days. On rendering alkaline the cold aqueous solution, either with ammonia or potassium hydroxide, a slow reaction set in, and after several days' intermittent shaking at the ordinary temperature, good yields of the hydroxylamino-oxime were produced. No oxime was obtained in these reactions, which will be described more fully in a later paper.

Further attention was thus directed to reaction in alcoholic or aqueous alcoholic solution. A solution of piperitone (10 grams) and hydroxylamine hydrochloride (5 grams) in methyl alcohol (40 c.c.), when kept at the ordinary temperature for a week, yielded a solid product (4·2 grams), which after crystallisation from light petroleum and ether melted at 113—114° (Found: N = 8·7. $C_{10}H_{17}ON$ requires N = 8·4 per cent.). The yield was depressed by the application of heat. When this method was modified by the

addition of sufficient alcoholic potassium hydroxide to render the solution alkaline, a small yield of the hydroxylamino-oxime, and no oxime, was obtained. When alcoholic sodium ethoxide was used for a like purpose, neither derivative was formed in appreciable quantity. The repetition of the original experiment of this series, with the addition of aqueous ammonia to render alkaline the methyl-alcoholic solution, resulted in the production of a small yield of the hydroxylamino-oxime, and no oxime. In all these instances the mixture was kept at the ordinary temperature for about a week. It is important to note that owing to the ready solubility of the oxime in dilute acid, an acid reaction mixture must be neutralised in order to render possible the complete isolation of the oxime.

From the evidence thus collected it appeared that the formation of oxime was favoured by (*a*) the presence of acid, (*b*) the use of aqueous alcohol as a solvent, and (*c*) the application of heat, except in strongly acid solution; whereas the formation of hydroxylamino-oxime was best effected by prolonged shaking of the ketone at the ordinary temperature with aqueous solutions of hydroxylamine containing an excess of alkali. It is to be observed that the latter conditions are such as to promote enolisation of the ketone.

The various specimens of oxime made in the ways indicated showed fluctuations in melting point and solubility. The crude product usually softened in the vicinity of 90° and was moderately soluble in boiling light petroleum and very soluble in ether. The recrystallised product, however, often melted at about 115° and was almost insoluble in light petroleum and only moderately soluble in ether. Eventually, a maximum melting point of 118—119° was attained for the α-oxime by further crystallisation from alcohol. Owing to the invariable presence of unchanged ketone in the mother-liquors, it proved impossible to isolate the more fusible β-oxime until the device was adopted of separating it by means of dilute mineral acid from the neutral, oily impurity. By correlating the data obtained in these preliminary experiments, the following method was finally elaborated for the preparation of these oximes:

dl-Piperitone (50 grams, $[\alpha]_D^{20} = -0{\cdot}50°$) was mixed with a 10 per cent. excess of hydroxylamine hydrochloride (25 grams) dissolved in water (50 c.c.). After the addition of just sufficient hot methylated spirit to give a homogeneous liquid, the acidity of the solution was depressed by the introduction of somewhat more than one equivalent of sodium acetate crystals (60 grams). The mixture was then heated under reflux on the water-bath for five or six hours, any turbidity being removed by the addition of methylated spirit. After allowing to stand over-night at the ordinary temperature,

most of the alcohol was removed by distillation from the water-bath. The semi-solid separation obtained on cooling and neutralising the residue with sodium carbonate was collected and washed with ether. The resulting hard, crystalline solid (20 grams) yielded pure α-oxime (14·5 grams), melting at 118—119°, after one recrystallisation from hot methylated spirit. The alcoholic mother-liquor was added to the aqueous filtrate from the above semi-solid separation, and the mixture was extracted with the ethereal washings of the same material. The resulting ethereal extract thus contained unchanged piperitone and the more soluble fraction of the oximes produced in the reaction. It was well shaken with two successive quantities of dilute sulphnric acid and finally with water; when dried and distilled from the water-bath, it yielded a residue consisting of unchanged piperitone (10·8 grams). When the sulphuric acid extract was carefully neutralised in the cold with sodium hydroxide solution, a solid crystalline precipitate (20·4 grams) was produced, melting indefinitely between 84° and 99°. On recrystallisation from hot absolute alcohol, this yielded successive fractions melting at 113—116° (11·2 grams), 89·5—91° (3·2 grams), 89·5—92° (3·3 grams), and 89—91° (1·0 gram). The last three fractions were obtained by slow evaporation of the solvent at the ordinary temperature, and consisted of almost pure β-oxime.

About 20 per cent. of the ketone was usually recovered unchanged in this reaction. The yield of recrystallised mixed oximes, calculated on the effective weight of ketone, approached 80 per cent. The mean ratio of the weights of recrystallised α-oxime and β-oxime obtained in a series of three preparations was 77 : 23.

dl-*Piperitone-α-oxime.*

Purified *dl*-piperitone-α-oxime is readily freed from traces of the more soluble β-oxime by recrystallisation from methyl or ethyl alcohol, but the final purification is difficult when light petroleum containing ether is used as solvent. The low melting point (110—111°) originally given for the substance is due to this fact. The pure α-oxime melts at 118—119° and is practically insoluble in light petroleum and only moderately soluble in ether. When allowed to separate slowly at the ordinary temperature from methyl or ethyl alcohol, in which it is readily soluble, it forms doubly terminated, stout prisms (Fig. 1), which exhibit high lustre and transparency. The crystals are often perfectly developed, but sometimes they show hour-glass structure and occasionally have striated prism faces. They are colourless, and vary in size up to about 3 cm. in length. The smaller crystals are generally the more perfectly developed; in many of the larger crystals some forms are suppressed. The faces

are bright, with a good lustre, and usually give satisfactory reflections. The forms present are *b*(010), *m*(110), *a*(100), *m'*(1$\bar{1}$0), *c*(001), *o*(0$\bar{1}$1), *d*($\bar{1}$01), and *e*($\bar{1}$11). Sometimes the crystals are slightly tabular on the *b*(010) face.

Crystal system.—Triclinic, normal.

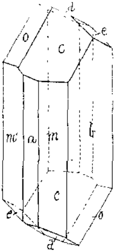
Axial ratios.—$a : b : c = 0{\cdot}7145 : 1 : 0{\cdot}5247$.

$\alpha = 68^\circ\ 10'$; $\beta = 112^\circ\ 34'$; $\gamma = 81^\circ\ 20'$.

Form.	No. of measurements.	Limits.*	Observed.		Calculated.	
		ϕ	ϕ	ρ	ϕ	ρ
b(010)	—	—	—	—	0° 00′	90° 00′
m(110)	14	48° 39′— 49° 02′	48° 52′	—	48° 50′	90° 00′
a(100)	12	81° 05′— 81° 22′	81° 11′	—	81° 11′	90° 00′
m'(1$\bar{1}$0)	14	119° 09′—119° 31′	119° 19′	—	119° 26′	90° 00′
c(001)	10	41° 11′— 41° 33′	41° 23′	32° 08′	41° 29′	32° 06′
o(0$\bar{1}$1)	6	103° 51′—104° 13′	104° 01′	23° 03′	103° 48′	23° 10′
d($\bar{1}$01)	8	47° 29′— 47° 44′	47° 38′	27° 07′	47° 37′	27° 12′
e($\bar{1}$11)	8	22° 28′— 22° 44′	22° 40′	44° 42′	22° 35′	44° 40′

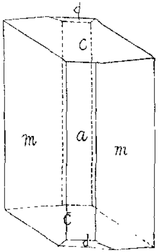
* The corresponding limits for ρ are: —, —, —, —, 31° 56′—32° 13′, 23° 01′—23° 10′, 27° 01′—27° 12′, and 44° 32′—44° 52′.

Fig. 1.



a-Oxime.

Fig. 2.



β-Oxime.

Large single crystals of the α-oxime exhibited no optical activity when dissolved in ethyl alcohol. The substance showed no tendency to form supersaturated solutions.

Through the kindness of Dr. Simonsen we were enabled, during the course of this work, to make a direct comparison between the oxime under consideration and the oxime of the same melting point prepared from the ketonic constituent of the essential oil of *Andropogon Jwarancusa* (T., 1921, **119**, 1652). The melting points of the separate preparations and of mixtures of the two were identical, namely, 118—119°. Moreover, after careful recrystallisation from ethyl alcohol, the Indian specimen exhibited the same crystalline

characteristics as the Australian α-oxime, as is evident from the appended summary of goniometric measurements :

Form.	Australian (calculated). ϕ	Indian (measured). ϕ	Form.	Australian (calculated). ϕ	Australian (calculated). ρ	Indian (measured). ϕ	Indian (measured). ρ
b(010)	0° 00′	0° 00′	c(001)	41° 29′	32° 06′	41° 14′	31° 59′
m(110)	48° 50′	48° 55′	o(0$\bar{1}$1)	103° 48′	23° 10′	104° 01′	23° 02′
a(100)	81° 11′	81° 06′	d($\bar{1}$01)	47° 37′	27° 12′	47° 33′	27° 08′
m′(1$\bar{1}$0)	119° 26′	119° 31′	e($\bar{1}$11)	22° 35′	44° 40′	22° 31′	44° 46′

dl-Piperitone-α-oxime remains solid in contact with boiling water, but is markedly volatile in steam. Its vapour has an odour very similar to that of menthol. The oxime is insoluble in water, but dissolves readily in dilute acids; it is precipitated unchanged from such solutions on the addition of alkalis, including ammonia. It is insoluble in dilute sodium hydroxide solution, and is not affected when the reagent is raised to the boiling point.

dl-*Piperitone*-β-*oxime*.

In spite of its low melting point and pronounced solubility, *dl*-piperitone-β-oxime crystallises without difficulty and shows no inclination to form supersaturated solutions. It dissolves with great ease in all the usual organic solvents, and may be recrystallised either from light petroleum or aqueous alcohol. After one recrystallisation from light petroleum, the crude product described above melted at 88—89°, and the melting point was not affected by further crystallisation. Slow deposition from this solvent gave well-developed crystals, which were somewhat smaller, as a rule, than those of the α-oxime (Found: N = 8·6. $C_{10}H_{17}ON$ requires N = 8·4 per cent.).

The crystals (Fig. 2) are colourless prisms, rarely doubly terminated, and having smooth bright faces. The prism zone is prominent, and consists of the forms *a*(100) and *m*(120). Sometimes the *a* form is wanting and the crystal assumes the shape of a four-sided prism. The *c* face is large and flat, the angle β approaching 90°. The negative ortho-prism is present as a small face, only occasionally yielding good reflections. There is an imperfect cleavage developed parallel to the *a*(100) face.

The forms developed are *a*(100), *c*(001), *m*(120) and *d*($\bar{1}$02).

Crystal system.—Monoclinic, holohedral.

Axial ratios.—*a* : *b* : *c* = 0·6670 : 1 : 0·6794. β = 93° 02′.

Angle.	No. of measurements.	Limits.	Observed.	Calculated.
am = 100 : 120	13	52° 55′—53° 13′	53° 06′	53° 06′
mm = 120 : $\bar{1}$20	7	73° 41′—73° 58′	73° 48′	73° 48′
ac = 100 : 001	6	86° 48′—87° 10′	86° 58′	86° 58′
cd = 001 : $\bar{1}$02	4	27° 26′—27° 42′	27° 35′	27° 35′

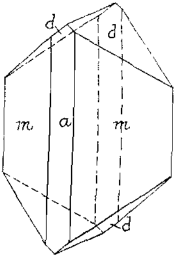
Individual crystals of this substance were optically inactive in alcoholic solution.

dl-Piperitone-β-oxime *liquefies in contact with boiling water, and* is readily volatile in steam. The odour of its vapour is similar to that recorded for the α-oxime, but is perceptibly sweeter. Like the α-oxime, it is soluble in dilute acids, but insoluble in water or sodium hydroxide solution. It is not affected by the last-named reagent when raised to the boiling point, and it is reprecipitated unchanged from its solution in dilute acid, or even in hot concentrated hydrochloric acid, on neutralisation.

dl-*Piperitone-α-oxime hydrochloride*, $C_{10}H_{16}$:NOH,HCl.

On passing dry hydrogen chloride into a solution of the α-oxime (5 grams) in benzene, a white, crystalline precipitate at once started to separate. The product (5·7 grams), after collection and washing with benzene, melted with decomposition at 157°, and the melting point was unaffected by recrystallisation. The characteristics of the new substance were those of the hydrochloride of a weak base. Although stable in dry air, it decomposed rapidly in water, yielding the original α-oxime and hydrochloric acid (Found, by titration, Cl = 17·0. $C_{10}H_{17}$ON,HCl requires Cl = 17·4 per cent.). It was readily soluble in alcohol, acetone, or chloroform, and by careful recrystallisation from a mixture of chloroform and benzene was obtained in well-developed crystals, which under favourable conditions often attained a moderate size. As usually obtained, the crystals were small and colourless. They possessed bright, smooth faces when first formed, but these often became pitted and lustreless, whilst the crystals also changed from transparent to opaque. Apparently these changes were due as much to the action of light as to that of moisture.

FIG. 3.



α-Oxime hydrochloride.

The forms exhibited by these crystals (Fig. 3) are the dominant prism, *m*(110); a narrow face, *a*(100), which is often suppressed; and the large brachy-domal prism, *d*(012).

Crystal system.—Rhombic, holohedral.

Axial ratios.—*a* : *b* : *c* : = 0·9088 : 1 : 1·5356.

Angle.	No. of measurements.	Limits.	Observed.	Calculated.
$mm = 110 : \bar{1}10$	14	95° 15′—95° 44′	95° 28′	95° 28′
$ma = 110 : 100$	6	42° 09′—42° 26′	42° 16′	42° 16′
$mm = 110 : 1\bar{1}0$	14	84° 19′—84° 43′	84° 32′	84° 32′
$dd = 012 : 0\bar{1}2$	10	74° 50′—75° 15′	75° 02′	75° 02′

The angle between the zones *dd* and *am* is 90°.

When *dl*-piperitone-α-oxime hydrochloride was decomposed by cold dilute sodium carbonate solution in presence of ether, it yielded exclusively *dl*-piperitone-α-oxime. An absolute alcoholic solution of the α-oxime gave no precipitate when added to a saturated alcoholic solntion of sodium ethoxide, and the oxime which was regenerated in qnantitative yield by the action of carbon dioxide melted unchanged at 118—119°.

The α-oxime thus exhibits no marked tendency to undergo transformation into the β-oxime; it is not only stable in the free state, but also forms a stable hydrochloride.

This heing the case, it was of particular interest to investigate the action of dry hydrogen chloride on the β-oxime. A strong solution of this isomeride in benzene remained perfectly clear after saturating it with the gas, but on warming the solution on the water-bath and keeping it over-night, a separation of the hydrochloride of the α-oxime occurred. When light petroleum was substituted for benzene, an immediate oily precipitate was formed; this crystallised when cooled in ice-water and rubbed with a little ether. On heating the product, it softened at about 120°, and melted completely with decomposition at 157°. In similar experiments, the crystalline product was shown to consist mainly of the hydrochloride of the α-oxime, and it appeared likely that the β-oxime formed a labile hydrochloride which underwent transformation into the stable isomeride.

p-*Nitrobenzoyl*-dl-*piperitone-α-oxime*, $C_{10}H_{16}{:}N{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$.

On mixing concentrated ethereal solutions of the α-oxime and *p*-nitrobenzoyl chloride, reaction occurred with ease. After keeping for several hours, the crystalline product was collected, washed with dilute hydrochloric acid and water, and purified by recrystallisation from hot alcohol, in which, as in most of the ordinary organic solvents, it was readily soluble. The aggregates of soft, opaque needles thus obtained melted at 126—127°. The yield was almost equal to the calculated amount (Found: N = 9·2. $C_{17}H_{20}O_4N_2$ requires N = 8·85 per cent.). The derivative was insoluble in hot dilute acid or alkali. When its solution (2 grams) in benzene was saturated with hydrogen chloride, a turbidity

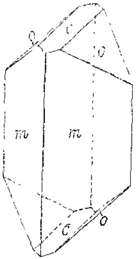
developed, followed by the separation of a heavy, oily layer. After standing over-night in an open vessel, most of the oil had disappeared, and the liquid contained crystalline material. When collected and washed with benzene and chloroform, this melted at 241° (corr.), and was identified as *p*-nitrobenzoic acid. The other product of the reaction was isolated as a dark brown oil; it contained chlorine (17·0 per cent.), was insoluble in dilute acid or alkali, and was possibly a chloro-derivative of menthoneoxime. It is thus evident that whilst *p*-nitrobenzoyl-*dl*-piperitone-α-oxime does not form a stable hydrochloride, it is readily hydrolysed under the conditions stated.

The m-*nitrobenzoyl* derivative, prepared in a similar way, crystallised from hot alcohol in small, colourless needles, melting at 104—105° (Found: N = 8·8 per cent.). The reaction was less rapid and complete than in the preceding instance.

The *benzoyl* derivative was similarly obtained as a colourless oil, which showed no tendency to crystallise, even after keeping for several months. A like result was achieved by the application of the Schotten-Baumann reaction and by the use of pyridine as a solvent for the reagents. When submitted to the action of hydrogen chloride in benzene solution, benzoyl-*dl*-piperitone-α-oxime underwent hydrolysis with the production of benzoic acid.

The β-*oxime* gave products identical with those just described, when allowed to react in ethereal solution with the three acid chlorides concerned. The reactions appeared to take place somewhat less readily than with the α-oxime, and the yields were not so high.

FIG. 4.



Dibromo-oxime.

Dibromo-dl-*piperitoneoxime.*

On brominating *dl*-piperitone-α-oxime in chloroform solution (Simonsen, *loc. cit.*, p. 1652), the halogen was absorbed only very slowly. After one recrystallisation from alcohol the product melted and decomposed at 124°, and even after repeated crystallisation it proved difficult to attain the recorded temperature of decomposition (141°). Different determinations made on the same specimen, even when the bath was preheated at 130°, gave results varying from about 133° to 140°.

Dibromo-*dl*-piperitoneoxime is not particularly stable in alcoholic solutions, which become red on prolonged keeping or continued warming. Purification may be effected more easily by recrystallisation from hot benzene. When allowed to separate slowly from alcoholic solutions, the pure

substance forms well-defined, colourless crystals (Fig. 4), which frequently possess some striated or rough faces, yielding indefinite reflections. The habit is prismatic, modified, however, by the presence of large smooth $o(011)$ faces, which are a feature of the crystals. The prism, $m(120)$, which is prominent, is often striated through irregular crystal growth. The $c(001)$ face, which is absent in some crystals, is a small narrow form, often giving blurred reflections. No cleavage was observed.

Crystal system.—Monoclinic, holohedral.

Axial ratios.—$a : b : c := 0{\cdot}6169 : 1 : 0{\cdot}9614$. $\beta = 99° 06'$.

Form.	No. of measurements.	Limits.* ϕ	Observed. ϕ	ρ	Calculated. ϕ	ρ
$m(120)$	15	39° 11′—39° 38′	39° 23′	—	39° 23′	90° 00′
$c(001)$	5	—	—	8° 56′	90° 00′	9° 06′
$o(011)$	7	9° 15′— 9° 36′	9° 27′	44° 16′	9° 27′	44° 16′

* The corresponding limits for ρ are : —, 8° 48′—9° 10′, and 44° 04′—44° 26′.

The β-oxime reacts much more rapidly with bromine than does the α-oxime. Under the conditions indicated above, instantaneous absorption of the halogen occurred during the first part of the reaction. The product, after recrystallisation, yielded the same dibromo-derivative as that prepared from the α-oxime and described above, the identity being established by melting point determinations and goniometric examination. Possibly, therefore, in view of the ease of reaction with bromine exhibited by the β-oxime, dibromo-*dl*-piperitoneoxime should be regarded as a derivative of the β-oxime rather than of the α-oxime. In both methods of preparation, the crude product appeared to contain a more soluble substance in association with the dibromo-derivative which has been described.

Dibromo-*dl*-piperitoneoxime is insoluble in dilute or concentrated hydrochloric acid. When warmed with dilute sodium hydroxide solution, the crystals assume a vivid emerald green colour, changing to yellow, and subsequently a brown oil is formed, sodium bromide being produced in the aqueous solution.

When a benzene solution of dibromo-*dl*-piperitoneoxime is saturated with dry hydrogen chloride and allowed to stand for several hours, clusters of colourless needles are deposited; these become pasty when exposed to the atmosphere, and appear to consist of an unstable hydrochloride.

We acknowledge our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of these researches, which are being continued.

DEPARTMENT OF ORGANIC CHEMISTRY,
UNIVERSITY OF SYDNEY. [*Received, February* 18*th*, 1922.]

LXIX.—*Production and Reactions of ββ′-Dichlorodiethyl Sulphide.*

By Frederick George Mann and William Jackson Pope.

The most convenient method of preparing ββ′-dichlorodiethyl sulphide, $(CH_2Cl{\cdot}CH_2)_2S$, furnishes a quantitative yield and consists in treating sulphur monochloride with ethylene (Gibson and Pope, T., 1920, **117**, 271). Under certain conditions (Mann, Pope, and Vernon, T., 1921, **119**, 634), the yield is not quantitative and the technical product is certainly far from pure. Gibson and Pope also showed that the sulphide can be obtained readily by the action of ethylene on sulphur dichloride, but that in this case the yield is only about 30 per cent. of that indicated by theory; the French have founded a technical process of manufacture on this reaction, using carbon tetrachloride as a diluent for the sulphur dichloride.

Many questions connected with the above two reactions are still under discussion, partly because too little experimental data are available for their decision and partly also because the various workers have not defined specifically the nature of the materials which they have used. We have already pointed out the difficulty of obtaining pure sulphur monochloride and it has been shown (Pope and Heycock, Eng. Pat. 142879, 1918) that sulphur dichloride only exists as a definite chemical individual under specific conditions. It seemed therefore desirable to study experimentally the action of the pure sulphur chlorides on ββ′-dichlorodiethyl sulphide and the related reactions between the latter substance and chlorine for the purpose of ascertaining the nature of the by-products which may accompany this organic compound.

It is now shown that on treatment with chlorine ββ′-dichlorodiethyl sulphide yields the corresponding tri-, tetra-, and hexachlorodiethyl sulphides, in each of which the further chlorine atoms introduced enter one only of the two ethylene residues of the molecule. This observation has some connexion with Regnault's work (*Ann. Chim. Phys.*, 1839, [ii], **71**, 392), which showed that diethyl ether yields a perchloro-derivative, $(C_2Cl_5)_2O$, on chlorination in sunlight; we have attempted to prepare perchlorodiethyl sulphide by the action of chlorine on ββ′-dichlorodiethyl sulphide in sunlight, but have merely obtained sulphur dichloride and perchloroethane in accordance with the reaction described below. It is interesting to notice that Riche (*Ann. Chim. Phys.*, 1855, [iii], **43**, 283) obtained a tetrachloro-, a hexachloro-, and an octachloro-diethyl sulphide by the chlorination of diethyl sulphide, and that by exhaustive chlorin-

ation in sunlight he obtained perchloroethane and a substance which he thought to be a perchlorodiethyl sulphide. Guthrie (*Quart. J. Chem. Soc.*, 1861, **13**, 35) described a tetrachlorodiethyl sulphide obtained by the action of ethylene on boiling sulphur monochloride, and converted it into a hexachlorodiethyl sulphide by direct chlorination; he presumed the latter to be identical with a hexachlorodiethyl sulphide which he obtained by the chlorination of diethyl sulphide. The boiling points and densities of the corresponding products now described differ so widely from those of the substances obtained by Riche and Guthrie as to make it improbable that we have been dealing with the same compounds. By the action of sulphur monochloride on ββ'-dichlorodiethyl sulphide we have obtained tri- and tetra-chlorodiethyl sulphide. The same products are formed on treating ββ'-dichlorodiethyl sulphide with sulphur dichloride, and in this case evidence has been also obtained of the formation of β-chloroethylsulphur chloride, $CH_2Cl\cdot CH_2\cdot SCl$.

When ethylene is passed through sulphur dichloride, the ruby-red colour of the latter gives place to an amber-yellow long before two molecular proportions of the hydrocarbon have been absorbed by one of the sulphur chlorides. If the reaction is arrested when the ruby-red colour disappears, a product is obtained from which no ββ'-dichlorodiethyl sulphide can be separated; it yields the tri- and tetra-chlorodiethyl sulphides and the β-chloroethylsulphur chloride together with the sulphur monochloride. It thus appears that the ββ'-dichlorodiethyl sulphide which Gibson and Pope obtained in about a 30 per cent. yield by the action of ethylene on sulphur dichloride is produced from the sulphur monochloride formed during the preliminary decoloration of the sulphur dichloride.

In practically all the chlorinations described in the present paper mixtures of several halogenated products are formed which cannot be resolved by ordinary fractional distillation under diminished pressure; by fractional distillation under 15 mm. pressure through the column which Dufton has recently described (*J. Soc. Chem. Ind.*, 1919, **38**, 45T) the product was in each case separated into its components without great difficulty. The new column is far more efficient than any which we had previously used, and we desire to direct attention to the fact that Dufton has devised a novel piece of apparatus which is of great service to the organic chemist.

Action of Chlorine on ββ'-Dichlorodiethyl Sulphide.

Chlorine is slowly but steadily absorbed when passed through ββ'-dichlorodiethyl sulphide; after a short time hydrogen chloride is evolved and the temperature rises to about 50°. Preliminary experiments in which one, two, three, and four molecules of chlorine

Ind., 1919, **38**, 469B; T., 1921, **119**, 645), but reaction does occur on prolonged contact of the two substances; the nature of the changes induced was therefore studied.

Carefully purified ββ'-dichlorodiethyl sulphide (23·85 grams) was mixed with sulphur monochloride (40·5 grams) free from iron, and the mixture allowed to remain at the ordinary temperature in absence of moisture; hydrogen chloride was slowly evolved and, after seventeen weeks, 9·75 grams of this gas had escaped and crystalline sulphur (5·45 grams) had separated. The yellow liquid (49·2 grams) was distilled, when sulphur monochloride (10·6 grams) came over below 75°/15 mm., followed by an oil (15·9 grams) boiling at 108—126°/15 mm.; much foaming, due to the evolution of hydrogen chloride, occurred during the distillation, and a black, tarry residue, consisting mainly of sulphur, remained. The oil boiling at 108—126° was separated by fractional distillation into trichlorodiethyl sulphide (8·0 grams) and tetrachlorodiethyl sulphide (5·8 grams).

On boiling ββ'-dichlorodiethyl sulphide (1 mol.) with sulphur monochloride (2 mols.) under a reflux, hydrogen chloride is slowly evolved, and after several hours an almost black liquid results; on distillation, a small yield of tetrachlorodiethyl sulphide is obtained (about one-fourth by weight of the original sulphide), whilst a heavy, black tar containing sulphur remains. The same result is obtained on heating the mixture at 100° for ten hours, when the evolution of hydrogen chloride ceases; a similar proportion of tetrachlorodiethyl sulphide and black tar results.

It thus appears that sulphur monochloride acts as a chlorinating agent on ββ'-dichlorodiethyl sulphide, slowly producing therefrom trichloro- and tetrachloro-diethyl sulphide at the ordinary temperature, and tetrachlorodiethyl sulphide in smaller yield at 100° or at the boiling temperature. The foaming which occurs during the distillation is probably due to the removal of hydrogen chloride from ββ'-dichlorodiethyl sulphide dichloride.

Action of Sulphur Dichloride on ββ'-Dichlorodiethyl Sulphide.

On adding sulphur dichloride, prepared by the method of Pope and Heycock, to ββ'-dichlorodiethyl sulphide at 0°, heat is evolved and the red colour of the sulphur dichloride is at once discharged; the liquid becomes yellow, smells of sulphur monochloride, and hydrogen chloride is evolved. As more dichloride is added, the action becomes less vigorous, and ultimately rapid stirring is necessary to discharge the red colour; about four molecular proportions of sulphur dichloride can be added before the red colour becomes persistent for a considerable time, but much of the reagent

is certainly carried away or decomposed by the escape of hydrogen chloride from the agitated liquid. Addition of a trace of iron hastens the action. When the product presenting the persistent red colour is distilled under reduced pressure, sulphur dichloride followed by sulphur monochloride comes over below 75°/15 mm., but distillation is rendered difficult hy the evolution of torrents of hydrogen chloride. By distilling small quantities at a time, a further distillate is obtained at 99—116°/14 mm.; this, on further fractionation and analysis, proves to he mainly trichlorodiethyl sulphide and tetrachlorodiethyl sulphide.

On heating the first reaction product at 150—160° under atmospheric pressure, hydrogen chloride is evolved and sulphur monochloride distils; when the dark red residue is distilled under reduced pressure, sulphur monochloride comes over below 75°/18 mm., followed by an orange-coloured fraction at 110—130°/18 mm. Just after condensation this fraction is nearly odourless, bnt on standing it soon evolves hydrogen chloride and acquires the odour of sulphur monochloride. This change in colour is prohably attributable to the presence of β-chloroethylsulphur chloride, $CH_2Cl{\cdot}CH_2{\cdot}SCl$. On treating the fraction with dilute nitric acid in order to oxidise the latter substance to β-chloroethanesulphonic acid, the residual oil, when distilled under reduced pressure through the Dufton colnmn, is resolved into trichloro- and tetrachlorodiethyl sulphides. The tarry residue left in the distillation of the crude product yields sulphur after boiling in benzene solntion with animal charcoal.

Consideration of the results described, which are typical of many others obtained, leads to the conclusion that the chief reactions concerned in the action of sulphur dichloride on ββ'-dichlorodiethyl sulphide are the following:

1. $(CH_2Cl{\cdot}CH_2)_2S + 2SCl_2 = CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl + S_2Cl_2 + HCl$.
2. $(CH_2Cl{\cdot}CH_2)_2S + S_2Cl_2 = CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl + 2S + HCl$.

With these is coupled the further chlorination to tetrachlorodiethyl sulphide.

Whilst the above represent the principal reactions of sulphur dichloride with ββ'-dichlorodiethyl sulphide, evidence has been obtained, as is noted above, that a certain proportion of β-chloroethylsulphur chloride is also formed. This substance could only result from the reaction expressed by equation 3, namely:

3. $(CH_2Cl{\cdot}CH_2)_2S + SCl_2 = 2CH_2Cl{\cdot}CH_2{\cdot}SCl$,

and it appears that reaction **3** is reversible under appropriate temperature conditions, yielding ββ'-dichlorodiethyl sulphide, which,

in presence of sulphur dichloride, yields trichlorodiethyl sulphide in accordance with equations 1 and 2. We are still occupied with the preparation in a pure state of β-chloroethylsulphur chloride and with the study of its properties. The production of β-chloroethylsulphur chloride seems to be proved by numerous experiments, of which the following may be quoted as typical.

Sulphur dichloride (305·8 grams) was gradually added during four hours, with constant stirring, to ββ'-dichlorodiethyl sulphide (71·3 grams), the temperature being maintained at 0°. Concentrated nitric acid (293 c.c., *d* 1·42) was then slowly added with cooling, when vigorous oxidation took place intermittently; after standing over-night, the mixture was run into water, the separated oil (54·0 grams) washed with water and very dilute sodium bicarbonate solution, dried, and distilled at atmospheric pressure. After repeated fractional distillation a colourless oil, which fumed slightly in the air and boiled at 198—204° under atmospheric pressure and at 93—97°/17 mm., was obtained. On analysis, this proved to be the β-chloroethanesulphonyl chloride, $CH_2Cl{\cdot}CH_2{\cdot}SO_2Cl$, described by Kolbe (*J. Chem. Soc.*, 1862, **15**, 97) as boiling at about 200° and by James (T., 1883, **43**, 42) as boiling at 200—205° (Found: Cl = 43·74; S = 19·33. Calc., Cl = 43·50; S = 19·67 per cent.). When this oil was repeatedly evaporated with the diluted nitric acid solution, the liquid treated with lead carbonate, and the filtrate evaporated, *lead* β-*chloroethanesulphonate* was obtained as a white powder (Found: C = 9·7; H = 1·4; Pb = 42·18. $C_2H_4O_3ClSPb$ requires C = 9·7; H = 1·6; Pb = 41·9 per cent.).

A further secondary reaction seems to accompany the action of sulphur dichloride on ββ'-dichlorodiethyl sulphide and results in the formation of diethylene disulphide. On agitating the crude product of the action of sulphur dichloride on ββ'-dichlorodiethyl sulphide with a paste of chalk and water in order to hydrolyse the chlorides of sulphur, extracting with ether, evaporating the ether extract, and treating the residue with nitric acid at 0° until no further oxidation occurs, the residual heavy oil, after washing and drying, gives on distillation the sulphonyl chloride boiling at 95—98°/16 mm., and a residue which yields a solid condensate when distilled under atmospheric pressure. This solid material crystallises from alcohol and is diethylene disulphide (Found: C=39·6; H=6·6. Calc., C = 39·9; H = 6·7 per cent.); it gives the characteristic blood-red coloration with nitric acid, and the quantity of pure product (1·5 grams) obtained from highly purified ββ'-dichlorodiethyl sulphide (54 grams) melting at 14° is so large as to preclude its having been present in the original materials.

Interaction of Ethylene and Sulphur Dichloride.

It has previously been shown (Gibson and Pope, T., 1920, **117**, 271) that on saturating sulphur dichloride with ethylene and distilling the product under reduced pressure a fraction is obtained which contains about 90 per cent. of ββ'-dichlorodiethyl sulphide and weighs about half as much as the sulphur dichloride used; this corresponds with a yield of about 30 per cent. of that which should be obtained in accordance with equation 4.

4. $2CH_2{:}CH_2 + SCl_2 = (CH_2Cl{\cdot}CH_2)_2S$.

On treating ethylene with sulphur dichloride, although not to completion, Guthrie (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116) obtained the unstable β-chloroethylsulphur chloride, and Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 590) concluded that they obtained the same substance by the action of sulphur dichloride on an excess of ethylene. For the purpose of elucidating the reaction between ethylene and sulphur dichloride we have carried out a number of experiments.

On passing a current of dry ethylene through strongly agitated sulphur dichloride maintained at 0°, the ruby-red colour of the dichloride changes to straw-yellow long before the proportion of ethylene absorbed attains that indicated in equation 4. When the product, obtained by passing in ethylene until the ruby-red colour is on the point of disappearing, is distilled under diminished pressure, a little sulphur dichloride comes over, followed by a considerable quantity of sulphur monochloride, both below 80°/15 mm.; much foaming, with evolution of hydrogen chloride, then occurs, and a fraction having the orange colour of β-chloroethylsulphur chloride distils at 95—130°/15 mm., and, lastly, a small fraction boiling at 150—160°/15 mm. A black tar remains in the distilling flask and this, as also the fraction distilling at 150—160°/15 mm., is instantly oxidised by nitric acid, giving β-chloroethanesulphonic acid. On agitating the fraction boiling at 95—130°/15 mm. with dilute nitric acid, to convert the β-chloroethylsulphur chloride into the sulphonic acid, a pale green oil remains, which is separable, by repeated fractionation through a Dufton column under reduced pressure, into about two parts of the trichlorodiethyl sulphide and one part of the tetrachlorodiethyl sulphide described above.

No evidence has been obtained of the presence of ββ'-dichlorodiethyl sulphide in the product which results from treating sulphur dichloride with ethylene up to the stage at which the dichloride itself disappears; the method of examining the product should have led to the detection of dichlorodiethyl sulphide, had this been present, because the chlorides of sulphur were distilled off rapidly

below 80°. During the distillation, little evolution of hydrogen chloride takes place before the sulphur chlorides have been volatilised and it thus appears that sulphur monochloride is present in the product before distillation.

The results obtained are in accordance with the view that several reactions occur simultaneously, namely, that indicated by Guthrie (5), followed by the conversion of β-chloroethylsulphur chloride into trichlorodiethyl sulphide, hydrogen chloride, and sulphur monochloride in accordance with 1 and 3.

The results obtained suggest that two reactions, represented by equations 5 and 6, occur simultaneously when ethylene is brought into contact with sulphur dichloride at 0°, namely:

5. $2CH_2{:}CH_2 + SCl_2 = (CH_2Cl{\cdot}CH_2)_2S$
6. $CH_2{:}CH_2 + SCl_2 = CH_2Cl{\cdot}CH_2{\cdot}SCl,$

and that at the low temperature reaction 5 is followed by that represented by equation 1, already shown to occur; after the sulphur chlorides have been distilled off, the product of reaction 6 decomposes in part in accordance with the reversal of reaction 3. A complication is introduced by further chlorination of trichlorodiethyl sulphide to give the tetrachloro-derivative. After the sulphur dichloride has disappeared, further absorption of ethylene occurs by the sulphur monochloride produced; if this follows the completion of reactions 5, 6, 1, and 2, the yield of ββ′-dichlorodiethyl sulphide should be 25 per cent. of that which would be obtained if reaction 5 proceeded alone. It has been shown, however, that some tetrachlorodiethyl sulphide is produced by further chlorination; the occurrence of this as a subsidiary reaction would increase the 25 per cent. yield; and, as has been noted, the total yield obtained by Gibson and Pope was about 30 per cent. of that possible from equation 5.

It has been stated by Conant and his colleagues (*loc. cit.*), that chlorination of the ββ′-dichlorodiethyl sulphide first formed can be prevented and a fairly pure sample of the latter obtained by treating dilute solutions of sulphur dichloride in carbon tetrachloride with ethylene.

Although the tri-, tetra-, and hexa-chlorodiethyl sulphides now described are more readily oxidised to the β-chloroethanesulphonic acid than is the dichloro-derivative, it was not found possible to prepare the corresponding sulphoxides and sulphones by the customary methods of oxidation. The sulphoxides of the tri- and tetra-chloro-compounds were obtained by the action of alkaline hypochlorite solutions on ββ′-dichlorodiethyl sulphoxide; the hexachlorodiethyl sulphoxide could not be obtained, and it appears

that the facility with which the sulphoxide is formed diminishes as the number of chlorine atoms in the molecule increases.

αββ'-Trichlorodiethyl Sulphoxide, $CH_2Cl{\cdot}CHCl{\cdot}SO{\cdot}CH_2{\cdot}CH_2Cl$.

ββ'-Dichlorodiethyl sulphoxide (50 grams) is mixed with sodium hydrogen carbonate (80 grams) and stirred up with sodium hypochlorite solution (500 c.c. containing 15 per cent. of available chlorine); vigorous action soon sets in and carbon dioxide is evolved. The mixture is cooled at 20° and filtered after two hours, the filtrate and residue extracted with chloroform, and the chloroform solution evaporated. The residual oil (32 grams) deposits crystalline ββ'-dichlorodiethyl sulphoxide (15 grams) and, after filtration of the latter, the oil is extracted with hot 30 per cent. alcohol; after heating on the water-bath and cooling, the remaining oil crystallises. The crystalline deposit is purified by crystallisation from carbon tetrachloride and proves to be *αββ'-trichlorodiethyl sulphoxide* (6 grams), which crystallises in long, colourless needles melting at 69° (Found: C = 22·8; H = 3·40; Cl = 50·82. $C_4H_7OCl_3S$ requires C = 22·9; H = 3·37; Cl = 50·77 per cent.). The compound is freely soluhle in benzene, chloroform, or alcohol, less soluble in ether, and nearly insoluble in cold water or carbon tetrachloride.

αβββ'-Tetrachlorodiethyl Sulphoxide, $CHCl_2{\cdot}CHCl{\cdot}SO{\cdot}CH_2{\cdot}CH_2Cl$.

The previous preparation is carried out so far as the cooling after the initial reaction with hypochlorite, and a large excess of hypochlorite solution is then added; after remaining over-night, the sludge is filtered by the aid of the pump, all oily products being drained away as completely as possible. The residue is washed with dilute hydrochloric acid, and the almost dry filter cake extracted with alcohol; on evaporating the alcoholic extract, a crystalline residue of the crude tetrachloro-compound is obtained, which is purified by crystallisation from boiling water. The substance separates from water in long, white needles melting at 121°; it is very soluble in alcohol or chloroform, less so in ether, and nearly insoluble in cold water (Found: C = 19·6; H = 2·5; Cl = 58·1. $C_4H_6OCl_4S$ requires C = 19·7; H = 2·5; Cl = 58·1 per cent.).

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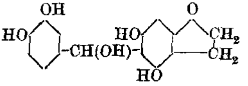
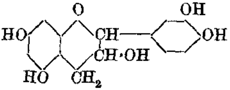
LXX.—*The Constitution of Catechin. Part IV.*

By MAXIMILIAN NIERENSTEIN

KOSTANECKI and LAMPE (*Ber.*, 1906, **39**, 4007; 1907, **40**, 4910) have shown that gambier-catechin tetramethyl ether yields with ease only mono-substituted halogen derivatives. On oxidation, these products give veratric acid, which was considered to be strong evidence in favour of the coumaran formula (A) for catechin, since the chroman formula (B) (A. G. Perkin and Yoshitake, T., 1902, **81**, 1172) requires disubstitution of the phloroglucinol nucleus.



(A.)

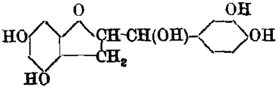


(B.)

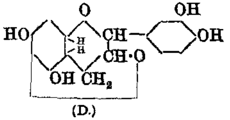
Kostanecki and Lampe's objection to formula B also applies to acacatechin tetramethyl ether (I) (compare T., 1921, **119**, 164), which has also been found to give a monobromo-derivative,* but the investigation of this bromo-derivative proves that the substitution takes place in the 3-position of the chroman ring and not in the phloroglucinol nucleus. The following evidence proves that *3-bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman* (II) is formed on bromination:

I. (*a*) 3-Bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (II) is quantitatively converted into *2-hydroxy-3:4:6:3′:4′-pentamethoxy-3-phenylchroman* (III) by boiling with methyl alcohol. The corresponding 3-ethoxy-derivative is obtained when ethyl alcohol is used instead of methyl alcohol. (*b*) On warming with

* The same objection holds good for the alternative formula C of Kostanecki and Lampe (*Ber.*, 1907, **40**, 720), which is now claimed by Freudenberg (*ibid.*, 1920, **53**, [*B*], 1416) as his alternative for formula B. Reference must be made to a recent modification of formula B by Euler (*Svensk. Kem. Tidskr.*, 1921, **33**, 88). His formula D is supposed to express the formation of monobromocatechin tetramethyl ether. It does not, however, account for the fact that catechin pentamethyl ether also yields only a monobromo-derivative (compare Kostanecki and Lampe, *loc. cit.*).



(C.)

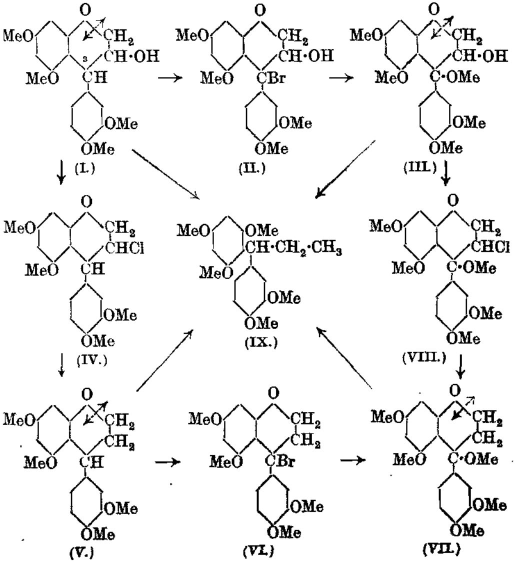


(D.)

zinc dust and alkali, the alcoholic solution gives acacatechin tetramethyl ether (I). Thus in all these properties it closely resembles α-bromodiphenylacetic acid (compare Meerwein, *Annalen*, 1913, **396**, 262) and other α-substituted bromo-derivatives (compare, for example, Hell and Bauer, *Ber.*, 1904, **37**, 232).

II. 2-Hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III) yields the same disintegration products (dimethylphloroglucinol and veratric acid) as acacatechin tetramethyl ether (I), which definitely proves that the new methoxy-group has not entered the phloroglucinol nucleus.

III. *Closely resembling acacatechin tetramethyl ether* (I), 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III) gives on reduction with metallic sodium and alcohol and subsequent methylation 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane (IX).



The following experiments prove that the substitution in acacatechin tetramethyl ether (I) does not take place in the 2-position.*

I. Acacatechin tetramethyl ether (I) is converted by the action of thionyl chloride into *2-chloro-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman* (IV), and subsequently reduced by Grignard and Tissier's method (*Compt. rend.*, 1901, **132**, 835) to *4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman* (V). The latter substance gives on bromination *3-bromo-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman* (VI), from which *3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman* (VII) is obtained by boiling with methyl alcohol.

II. 3 : 4 : 6 : 3′ : 4′-Pentamethoxy-3-phenylchroman (VII) is also obtained by converting 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III) into *2-chloro-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman* (VIII) and subseqnent reduction by Grignard and Tissier's method.

It is found that both 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (V) and 3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (VII) give 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane (IX) on reduction with metallic sodium and alcohol and subsequent methylation.†

Reference must be made to a publication by Freudenberg, Böhme, and Beckendorf (*Ber.*, 1921, **54**, [*B*], 1204), who claim to have established the identity of Kostanecki and Lampe's methylated reduction product (*Ber.*, 1907, **40**, 720) with synthetic 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αγ-diphenylpropane. In support of this contention, they quote the absolute identity of the melting points and the crystallographical data of these two substances. This is contrary to the author's previous observations (T., 1920, **117**, 1156) as regards the melting points and mixed melting points of 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane (m. p. 83—84°), 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αγ-diphenylpropane (m. p. 87—88°), and Kostanecki and Lampe's methylated reduction product (m. p. 83—84°). It is also contrary to the crystallographical observations of Mr. T. V. Barker, who kindly undertook the investigation and who reports (July 18th, 1921) as follows :

* Monosubstitution in the 1-position is very improbable. It is, however, intended to investigate this point and to revert to it at a later date.

† It is not proposed to give the experimental details of the reduction and subsequent methylation of either of these substances or of 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III). All these processes were carried out exactly as described by Kostanecki and Lampe (*Ber.*, 1907, **40**, 720), and reference to them has been made in previous papers by the author (T., 1920, **117**, 971, 1151 ; 1921, **119**, 164). All the methylated reduction products obtained from these substances melted at 83—84°, which melting point was not depressed on admixture with synthetic 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane.

"Three specimens were sent by Dr. Nierenstein for examination, labelled respectively 'Kostanecki's methylated reduction product' (hereafter termed 'A'), 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane ('B'), and 3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αγ-diphenylpropane. A crystallographical examination proves the identity of 'A' and 'B.' They both crystallise in very strongly double-refracting 64°-rhombic plates or leaflets, which rarely develop an additional edge (apparently due to cleavage). The vibration direction of the slower ray makes an angle of 4° with one edge, the faster being inclined at an angle of 22° with the other edge. One of the two refractive indices is close to that of olive oil, so that a remarkable change of relief is observed when an immersed fragment is rotated over the polariser. Nothing characteristic is seen in convergent light.

"The αγ-derivative is different from 'A' and 'B.' It crystallises in lustrous, flattened needles with straight extinction and a relatively weak double refraction. No change of relief is noticeable when examined in olive oil. In convergent light the normal to the flattened facet is seen to be the acute bisectrix of an optically negative crystal. The axial plane contains the direction of elongation, and the optical axial angle is wide.

"Observations prove that neither 'A' nor 'B' has the power of causing the crystallisation of a supersaturated alcoholic solution of the more soluble αγ-isomeride. These results disprove any possibility that the difference in optical properties is due to a difference of orientation, and are scarcely reconcilable with a view that the two specimens are dimorphous forms of the same chemical species.

"The result of this comparative examination, then, is to prove that the 'Kostanecki methylated reduction product' is identical with *3 : 4 : 2′ : 4′ : 6′-pentamethoxy-αα-diphenylpropane* and different from the specimen of the αγ-isomeride of the latter. These results, it must be noted, are not in agreement with those of a recent trustworthy examination by Steinmetz of two preparations submitted to him by Freudenberg, Böhme, and Beckendorf (*Ber.*, 1921, **54**, [*B*], 1208) as being Kostanecki's methylated reduction product and the αγ-derivative. The two preparations were found by Steinmetz to be crystallographically identical, both crystallising in plates, which the present writer finds to have a superficial, geometrical resemblance to the substances 'A' and 'B,' but not in the angular values nor in the optical details. A double discrepancy is involved in the results of the various crystallographical examinations, for neither Steinmetz's 'Kostanecki product' nor his αγ-isomeride is identical with those examined by the present writer,

who has come to the conclusion that, owing to some error or other, the reputed $\alpha\gamma$-isomeride submitted to Steinmetz may really have been a second specimen of the German chemists' 'Kostanecki product' (whatever that was) and not authentic $\alpha\gamma$-material. The reason for this belief is that Freudenberg's original description (*Ber.*, 1920, **53**, [*B*], 1427) of the $\alpha\gamma$-compound ('lustrous, colourless, very thin, needle-shaped, elongated rectangles') is a fair description of the $\alpha\gamma$-material submitted to the present writer, but can scarcely be identified with either of the two specimens subsequently sent to Steinmetz for examination—for structural considerations teach the truth that the needle is the crystallographical antipode of the leaflet or plate and cannot be expected to vary its form with change of solvent or of the physical conditions attending the act of crystallisation."

EXPERIMENTAL.

The acacatechin used in this investigation was prepared according to the method described by Perkin and Yoshitake (*loc. cit.*, p. 1169). It was crystallised from distilled water slightly acidified with acetic acid. Two different specimens of *Acacia catechu* extract were used for the preparation of acacatechin, for which the author is indebted to the Director of the Imperial Institute and the Director of Agriculture for India respectively. The acacatechin from both sources melted at 204—205°, as given by Perkin and Yoshitake. Several preparations were also made according to the method of Freudenberg, Böhme, and Beckendorf (*loc. cit.*, p. 1208), they also melted at 204—205°; and all attempts to isolate a specimen melting at 216—218°, as given by Freudenberg and his collaborators, have failed. This is of interest since Perkin and Yoshitake were also unable to obtain a specimen, which melted at 217°, as given by Zwerner (*Annalen*, 1841, **37**, 320). An average yield of 76 per cent. on the extract was obtained by Perkin and Yoshitake's method, whereas Freudenberg's method gave only 32 per cent., which is slightly higher than the quantity found by him (20—25 per cent.). Preliminary experiments, both with acacatechin and the penta-acetyl derivative, showed that neither of the two acacatechin preparations was optically active.* This is also contrary to the results of Freudenberg and his collaborators (*loc. cit.*), who find that their specimen of acacatechin is a mixture of *dl*- and *l*-catechin.†

* For these observations I am indebted to Mr. R. Barr, B.Sc.

† The question of the optical activity of acacatechin and Freudenberg's criticism (*Z. angew. Chem.*, 1921, **34**, 247) of my synthesis of this substance,

Acacatechin tetramethyl ether was prepared according to A. G. Perkin's method (T., 1905, **87**, 400). It melted at 152—154° and gave the indigo-blue coloration with acetic acid and nitric acid described by Perkin. Reference has been previously made (T., 1921, **119**, 168) to the fact that synthetic acacatechin tetramethyl ether does not give this colour reaction, and it was therefore at the time suggested that the colour was probably due to a trace of another substance. This seems to be the case, as may be judged from the following experiment.

To a solution of 2 grams of acacatechin tetramethyl ether in 25 c.c. of glacial acetic acid is added 1 c.c. of nitric acid, when a deep indigo-blue coloration is immediately produced. After standing for twenty-four hours, the colour disappears completely, and the solid obtained on precipitation with water is crystallised from alcohol, from which it is deposited in small, prismatic needles, melting at 154° (mixed m. p. with the synthetic product, 154°). The purified product does not give this characteristic coloration. It is interesting to note that gambier-catechin tetramethyl ether behaves exactly in the same manner. The tetramethyl ether of Perkin and Yoshitake's high-melting gambier-catechin (*loc. cit.*, p. 1167), even after repeated purification by the method just described, yields no product which does not give the Perkin coloration. It is therefore possible that this reaction is due to traces of the high-melting gambier-catechin, since from observations made in this laboratory high-melting catechin is found, not only in cube gambier (Perkin and Yoshitake, *loc. cit.*), but also in *Acacia catechu* extract.

3-Bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (II).

To a solution of 20 grams of acacatechin tetramethyl ether in 50 c.c. of glacial acetic acid 9 grams of bromine dissolved in the

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which he bases on the supposed optical activity of acacatechin, are under investigation and will be dealt with in a later communication.

In this connexion it is interesting to note that both catechu extract and cube-gambier are known to contain sugars (compare Schroeder, "Gerberei-Chemie," 1898, p. 613), which, perhaps, explains Freudenberg's observations as regards the optical activity of his preparations of aca-, and gambier-catechin. It has already been shown, in the case of paullinia tannin (this vol., p. 27), which easily gives gambier-catechin, that this tannin is a glucoside, and it is therefore quite possible that Freudenberg's method of purification, which does not exclude tannins, introduces such optically active by-products into his catechin preparations. To judge from my experience with paullinia tannin and also from the literature on the manufacture of catechu extract and cube-gambier (compare Harwey, "Tanning Materials," 1921, p. 27) I am certain that the catechins present in those extracts are mainly racemised, which is in agreement with my previous observations on the optical activity of gambier-catechin (*Annalen*, 1913, **396**, 194).

same solvent are added. The solid formed on standing in diffused sunlight crystallises from glacial acetic acid in colourless needles, which melt at 191—192°. The product is also soluble in alcohol and acetone, from which it crystallises in the same manner. The melting point of the bromo-derivative, when crystallised from alcohol, is, however, lower and not sharp. An average theoretical yield was obtained from three different preparations (Found : * C = 53·5 ; H = 5·3 ; Br = 19·0. $C_{19}H_{21}O_6Br$ requires C = 53·6 ; H = 5·0 ; Br = 18·8 per cent.).

2-Hydroxy-3 : 4 : 6 : 3′ : 4′-*pentamethoxy*-3-*phenylchroman* (III).

Twenty-five grams of 3-bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (II), dissolved in 700 c.c. of methyl alcohol, which has been dried over calcium oxide, are boiled under reflux for thirty hours. On cooling, no solid is formed, which indicates the end of the reaction, since 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman is about ten to twelve times more soluble in methyl alcohol than the bromo-product. The solid formed on precipitation with water crystallises from dilute alcohol in prismatic needles, which melt at 163—164°. The product is soluble in the usual organic solvents. Three different experiments were made, all of which gave a theoretical yield [Found : † C = 63·9 ; H = 6·6 ; OMe = 41·4, 41·3. $C_{15}H_9O_2(OMe)_5$ requires C = 63·8 ; H = 6·4 ; OMe = 41·2 per cent.]. On digestion with acetic anhydride, the *monoacetyl* derivative is easily obtained. It crystallises from alcohol in needles, which melt at 147—148° (Found : ‡ C = 63·0 ; H = 6·4. $C_{22}H_{26}O_6$ requires C = 63·2 ; H = 6·2 per cent.). When methyl alcohol is replaced by absolute ethyl alcohol, the corresponding *2-hydroxy*-4 : 6 : 3′ : 4′-*tetramethoxy* - 3 - *ethoxy* - 3 - *phenylchroman* is formed. It crystallises from dilute alcohol in small needles, which melt at 168° (Found : ‡ C = 64·7 ; H = 6·8. $C_{21}H_{26}O_7$ requires C = 64·6 ; H = 6·7 per cent.). In this connexion it is interesting to note that Krembs (*Diss.*, Bern, 1903, p. 27) seems to have found difficulty in crystallising monobromo-gambier-catechin tetramethyl ether from alcohol. This was probably due to partial elimination of the bromine during the process of crystallisation from alcohol. All experience made in this laboratory points to the fact that the different monobromo-derivatives are best crystallised from glacial acetic acid.

2-Hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman, when oxidised with potassium permanganate as described by Perkin (*loc. cit.*, p. 401) in the case of acacatechin tetramethyl ether, gives also an acidic and a phenolic disintegration product, both of which are

* Dried at 100°. † Dried at 100° in a vacuum. ‡ Dried at 100°.

identical with those obtained by Perkin from acacatechin tetramethyl ether; this experiment was also repeated by the author. The acidic product is veratric acid (m. p. and mixed m. p. 179°) (Found: C = 59·1; H = 5·7. Calc., C = 59·4; H = 5·5 per cent.). The phenolic substance, a colourless, semi-crystalline mass, gives, on crystallisation from benzene and light petroleum, a very small quantity of product melting at 37°. This is the melting point given by Pollak for dimethylphloroglucinol (*Monatsh.*, 1897, **18**, 737). For further identification the whole product left on evaporation of the benzene and light petroleum is redissolved in ether and methylated with diazomethane. The product left on evaporation of the ether crystallises in long needles from light petroleum, after standing over ice for some time. This product melts at 52°, which melting point is not depressed on admixture with authentic trimethylphloroglucinol. There was not enough material for combustion.

Both 3-bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (*II*) and 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III) are easily converted into acacatechin tetramethyl ether (I). Kostanecki and Lampe (*loc. cit.*, p. 4910) have already observed a similar transformation in the case of monobromogambier-catechin tetramethyl ether, from which they recovered unchanged gambier-catechin tetramethyl ether.

To a solution of 5 grams of either substance II or III in 50 c.c. of alcohol, 10 c.c. of a 50 per cent. solution of potassium hydroxide and 20 grams of zinc dust are added. The solution is heated on a water-bath for three hours, filtered when cold, and water added to the filtrate. The solid thus obtained is crystallised several times from dilute alcohol, from which it crystallises in small, prismatic needles, which melt at 154°. This melting point is not depressed on admixture with synthetic acacatechin tetramethyl ether. Acacatechin tetramethyl ether, recovered in this manner from the *bromo-product, does not give the Perkin coloration* (*Found*: C = 66·0; H = 6·6. Calc., C = 65·9; H = 6·3 per cent.).

2-*Chloro*-4 : 6 : 3′ : 4′-*tetramethoxy*-3-*phenylchroman* (IV).

Five grams of acacatechin tetramethyl ether, dissolved in 50 c.c. of dry benzene, and 15 grams of thionyl chloride are heated on a water-bath for three hours and the unchanged thionyl chloride and also the benzene distilled off in a vacuum. The remaining solid is warmed with 2 c.c. of anhydrous formic acid and dried in a vacuum over solid sodium hydroxide for some time. The product is very *soluble in the usual organic solvents, but crystallises in small cubes* from a mixture of one part of benzene and two parts of light petroleum. It melts sharply at 116°. The average yield of three

preparations is 78 per cent. of the theoretical (Found: * C = 62·3; H = 6·1; Cl = 10·1, 9·9. $C_{19}H_{21}O_5Cl$ requires C = 62·6; H = 5·8; Cl = 9·8 per cent.).

4 : 6 : 3′ : 4′-*Tetramethoxy-3-phenylchroman* (V).

Twelve grams of the chloro-derivative (IV), dissolved in 750 c.c. of dry ether (Grignard), and 1·5 grams of "activated" magnesium (Baeyer, *Ber.*, 1905, **38**, 2759) are heated on a water-bath, when the solution will become deep-red in about forty minutes, from which point the solution is heated for another two hours. The solid left on distillation of the ether is treated with ice and hydrochloric acid. It is then dissolved in alcohol and precipitated with water, the process being repeated several times. The product then crystallises in small cubes from alcohol, which melt at 94°. The substance is soluble in the usual organic solvents. It may also be crystallised from dry benzene. The average yield of two preparations is only 67 per cent. of the theoretical; this is due to the formation of a by-product, which is sparingly soluble in alcohol [Found: † C = 68·8; H = 7·1; *M* (in benzene) = 316, 328, 330. $C_{19}H_{22}O_5$ requires C = 69·1; H = 6·7 per cent.; *M* = 330].

An experiment to reduce the chloro-derivative (IV) by Zelinsky's method (*Ber.*, 1898, **31**, 3205) gave only 15 per cent. of 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (m. p. 94°, which was not depressed on admixture with the product prepared by Grignard and Tissier's method). The main product obtained by Zelinsky's method crystallised from dilute acetic acid in needles which melted at 218°. This substance is probably polymerised 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (Found: C = 68·7; H = 6·9. Calc., C = 69·1; H = 6·7 per cent.). As already mentioned, a similar by-product is also formed by Grignard and Tissier's method; the two substances can be separated from 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman by repeated extraction with hot alcohol, in which the polymerised substances are only sparingly soluble.

3-*Bromo*-4 : 6 : 3′ : 4′-*tetramethoxy-3-phenylchroman* (VI).

Ten grams of 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (V), dissolved in 25 c.c. of glacial acetic acid, are treated with 4·5 grams of bromine in 10 c.c. of the same solvent. The solid obtained on allowing the solution to remain in an open dish for some time crystallises from dilute acetic acid in small needles, which melt with decomposition at 147—149° (Found: Br = 20·1. $C_{19}H_{21}O_5Br$

* Dried in a vacuum over paraffin.

† Dried in a vacuum over phosphoric oxide.

requires Br = 19·5 per cent.). On boiling the alcoholic solution of the substance (2 grams) with alkali (5 c.c. of 50 per cent. sodium hydroxide) and zinc dust (5 grams), 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (V) is produced (m. p. and mixed m. p. 94°) (Found : C = 69·1; H = 6·9. Calc., C = 68·8; H = 7·1 per cent.).

3 : 4 : 6 : 3′ : 4′-*Pentamethoxy-3-phenylchroman* (VII).

Ten grams of the bromo-derivative (VI) are treated with dry methyl alcohol in exactly the same manner as 3-bromo-2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (II). The resulting 3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (VII) crystallises from alcohol in star-shaped needles, which melt at 127°. A theoretical yield is obtained (Found :* C = 66·3; H = 6·9. $C_{20}H_{24}O_6$ requires C = 66·7; H = 6·7 per cent.).

2-*Chloro*-3 : 4 : 6 : 3′ : 4′-*pentamethoxy-3-phenylchroman* (VIII).

Ten grams of 2-hydroxy-3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (III), dissolved in 50 c.c. of dry benzene, and 30 grams of thionyl chloride are heated on a water-bath for three hours and subsequently treated in the manner previously described for the preparation of 2-chloro-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman (IV). The product crystallises from dry benzene in long, pointed needles, which melt sharply at 97°. The yield is 74 per cent. of the theoretical (Found : Cl = 8·8, 8·5. $C_{20}H_{23}O_7Cl$ requires Cl = 8·6 per cent.).

This chloro-derivative (3 grams dissolved in 250 c.c. of dry ether) is readily reduced to 3 : 4 : 6 : 3′ : 4′-pentamethoxy-3-phenylchroman (VII) with the aid of 0·7 gram of "activated" magnesium, the procedure being the same as previously described. Both its melting point and mixed melting point are at 127° (Found : C = 66·4; H = 7·0. Calc., C = 66·7; H = 6·7 per cent.).

In conclusion, the author wishes to thank Mr. T. V. Barker, M.A., for the trouble he has taken in preparing his crystallographical report, and the Research Fund Committee of the Chemical Society for a grant, which has covered the expenses of this research.

* Dried at 100°.

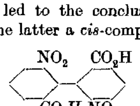
THE UNIVERSITY, BRISTOL. [*Received, February 17th,* 1922.]

LXXI.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part I. The Resolution of γ-6:6′-Dinitro- and 4:6:4′:6′-Tetranitro-diphenic Acids into Optically Active Components.*

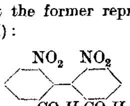
By George Hallatt Christie and James Kenner.

It has usually been considered that the benzene nuclei of the two phenyl residues contained in diphenyl and its derivatives are coplanar. It was suggested, however, by Kaufler (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250, 3253) that, on the contrary, the two nuclei are situated in two parallel planes. The evidence in favour of this view (Kaufler, *loc. cit.*; Cain and Micklethwait, T., 1914, **105**, 1437; compare Turner, T., 1915, **107**, 1495) rested on the formation of cyclic compounds from benzidine analogous to those obtainable from *o*-diamines. It has been pointed out, however, that even if this evidence be accepted at its face value, the only inference strictly permissible from it is that the Kaufler formula represents a configuration which diphenyl may assume under certain conditions, but is not necessarily its normal one (Kenner and Mathews, T., 1914, **105**, 2473). It is therefore evident that a real decision in regard to the accuracy of Kaufler's formula is not to be attained in this way.

A more definite contribution to the question has, however, become possible since the discovery of a γ-form of 6:6′-dinitrodiphenic acid (Kenner and Stubbings, T., 1921, **119**, 593), distinct from the β-acid already known. A discussion of the reactions of these two compounds led to the conclusion that the former represented a *trans*- (I), the latter a *cis*-compound (II):



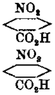
(I.)

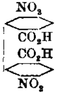


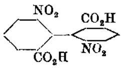
(II.)

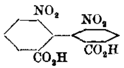
A consideration of these formulæ from the stereochemical point of view shows that, on the basis of the plane formula for diphenyl, the *cis*-form possesses a plane of symmetry, whilst the *trans*-form has a centre of symmetry, and that therefore neither form should be resolvable into optically active components. On the other hand, the Kaufler formulæ (or any similar ones, in which the planes of the two benzene nuclei are not parallel, but equally inclined to a third plane) suggest that, whilst the *cis*-compound (III) again possesses a plane of symmetry, the *trans*-form (IV) is not superimposable on its mirror image, and should therefore be capable of

resolution. Another possibility—and one at first sight perhaps more acceptable from the point of view of strain on the carbon


(III.)


(IV.)


(V.)


(VI.)

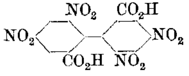
atoms by which the two nuclei are united—is that the two benzene nuclei possess a common axis, but do not lie in the same plane. In this case, it will be seen that both forms of the acid (V and VI) should be resolvable. The limiting case of this kind, in which the planes of the two nuclei are at right angles, is at once excluded, since it allows the existence of only one form of 6 : 6′-dinitrodiphenic acid. There is a fourth possibility, representing a combination of the two preceding ones, that the planes of the two benzene nuclei possess neither an axis nor a plane of symmetry. Quite apart from the increased isomerism demanded by this arrangement, it seems inherently improbable that the diphenyl system should not possess any element of symmetry, and therefore attention may for the present be concentrated on the simpler conceptions.

It has now been shown that γ-6 : 6′-dinitrodiphenic acid furnishes two brucine salts, of which approximately equal quantities were separated by fractional crystallisation.* The two salts are distinct in regard to their solubilities, crystalline forms, degrees of hydration, melting points, and rotatory power. It was to be anticipated that the usual methods for the liberation of optically active acids from their brucine salts would not be very efficient in the case of the sparingly soluble salts of such a strong acid as dinitrodiphenic acid. Experiment showed that the yields of the active acids obtainable in this way are poor, and this, together with the facts that they *are appreciably more soluble in water than the inactive racemic* acid, and exhibit a distinct tendency to racemisation, has prevented the attainment of constant values of their rotatory power. Nevertheless, those so far observed ($[\alpha]_D^{25^\circ}$ + 225° for the acid from the

* The possibility of resolving either the β- or the γ-acid has also been queried by Thorpe in a review of the late Dr. Cain's work (Obituary Notice, T., 1921, **119**, 535). Further, since the present paper was read before the Society, Dr. H. King has directed our attention to his paper on "The Possibility of a New Instance of Optical Activity without an Asymmetric Carbon Atom" (P., 1914, **30**, 250), in which it is pointed out that if the Kaufler formula holds, 3 : 5′-, but not 3 : 3′-dinitrobenzidine should be resolvable. The appearance of the paper at a time when I was out of touch with chemical literature, and the absence of any reference in the title to diphenyl had caused us to overlook it.—J.K.

less soluble salt, and $-169{\cdot}7°$ for that from the more soluble salt) are such as leave no doubt as to their activity. The melting points, 230—231° and 230—238°, respectively, also distinguish them from the racemic acid, which melts at 263°.

Further, 4 : 6 : 4′ : 6′-tetranitrodiphenic acid (VII) has been pre-



(VII.)

pared by the nitration of 4 : 4′-, and of β- and γ-6 : 6′-dinitrodiphenic acids separately. In each case, the nitration product itself, and its methyl and ethyl esters, were found to be identical with those synthetically obtained from 2-chloro-3 : 5-dinitrobenzoic acid (Ullmann and Engi, *Annalen*, 1909, **366**, 79). From this acid also, two brucine salts, distinct in the same respects as those derived from racemic γ-6 : 6′-dinitrodiphenic acid, were obtained. Since it seemed probable that even greater difficulty than in the case of the dinitrodiphenic acids would be encountered in preparing the active tetranitrodiphenic acids from their salts, it was decided to attempt a direct resolution by treatment of the racemic acid with half the quantity of brucine necessary for complete neutralisation (compare Pope and Peachey, T., 1899, **75**, 1066). By this means, the acid corresponding with the more soluble brucine salt was isolated and found to have $[\alpha]_D^{16}$ $-19{\cdot}28°$. Probably, in this case also, racemisation occurred, but it will be noticed that the sign of the rotation agrees with that of the form of γ-dinitrodiphenic acid derived from the more soluble brucine salt. Here again, the active acid is appreciably more soluble than the inactive form, and its melting point is lower.

Whilst, therefore, further work may somewhat modify the actual values quoted for the rotation constants, the fact of the resolvability of the two acids is completely demonstrated, and it would seem to follow that their molecular structure is such that the two benzene nuclei are not coplanar. An examination of β-6 : 6′-dinitrodiphenic acid will enable a decision to be reached between the two more probable alternatives which satisfy this condition. It may be stated, however, that 4 : 4′-dinitrodiphenic acid furnishes only one brucine salt, a fact which suggests that the Kaufler type of formula is more probable than the one in which two benzene nuclei possess a common axis.

Some of the isomeric diphenyl compounds examined by Cain may also prove to be capable of resolution, and a number of other diphenic acids are in course of examination in this laboratory. It will also be germane to the present work to ascertain whether the

absence of free rotation of the two benzene nuclei in the diphenyl derivatives above discussed is reproduced in derivatives of diphenylmethane and -ethane, since these are ordinarily represented by formulæ very similar to the Kaufler diphenyl formula. It will also be recalled that Kaufler suggested that the two benzene nuclei in naphthalene are not coplanar. A consideration of model formulæ of this type shows that, on this basis, a large number of naphthalene derivatives should be capable of resolution into optically active forms. It is therefore hoped to obtain a decision in this direction also.

EXPERIMENTAL.

Resolution of γ-6 : 6′-Dinitrodiphenic Acid.

To a boiling aqueous solution of the acid (6 grams), finely ground anhydrous brucine (14·25 grams) was gradually added, the solution being diluted, as required, to 3750 c.c. to maintain the salts in solution as they were produced. On cooling, a uniform crystallisation of the less soluble salt was obtained in four-sided plates. At a later stage, when the total bulk had been redneed to 1275 e.c., radiate clusters of plates appeared on cooling the solution, and a further small quantity was obtained after concentration to 990 c.c. Yet more of the salt, less pure, was obtained by further evaporation. After purification by repeated crystallisation, an average yield of 8·5 grams of the less soluble, and 6 grams of the more soluble, salt was obtained.

Brucine d-γ-6 : 6′-*dinitrodiphenate*,

$$C_{12}H_6(NO_2)_2(CO_2H)_2,2C_{23}H_{26}O_4N_2,8\frac{1}{2}H_2O,$$

the less soluble of the above salts, melts and decomposes at 261°; for the anhydrous salt, $[\alpha]_D = +61{\cdot}2°$ in 1·68 per cent. chloroform solution. For a second specimen, obtained from a different sample of brucine and another preparation of the acid, $[\alpha]_D = +60{\cdot}42°$ in 2·55 per cent. chloroform solution. One part dissolves in approximately 375 c.e. of boiling water, and in 3750 c.c. at the ordinary temperature. Analyses were made both of the hydrated salt (Found: N = 6·87; H_2O = 11·90. $C_{60}H_{60}O_{16}N_6,8\frac{1}{2}H_2O$ requires N = 6·60; H_2O = 12·00 per cent.) and of the anhydrous compound, dried at 120° (Found: C = 64·21; H = 5·60; N = 7·71. $C_{60}H_{60}O_{16}N_6$ requires C = 64·28; H = 5·36; N = 7·5 per cent.).

d-γ-6 : 6′-*Dinitrodiphenic Acid*, $C_{12}H_6(NO_2)_2(CO_2H)_2$.—To a solution of the brucine salt (3·15 grams) in water (1200 c.c.), which had been cooled until, at 45°, crystallisation had just set in, excess of dilute sulphuric acid (2*N*, 100 c.c.) was added. The cold solution was repeatedly extracted with ether, and the ethereal extract washed first with dilute sulphuric acid until the washings gave no coloration

when tested with nitric acid, and finally with water. The acid obtained by evaporation of the ethereal solution, after the latter had been dried over anhydrous sodium sulphate, was further purified by solution in *N*/5-ammonia (30 c.c.), and reprecipitation with dilute sulphuric acid. The product thus obtained (0·27 gram) melted at 230—231° (as compared with 263° for the melting point of the inactive acid), and had an equivalent of 166·9 [$C_{12}H_6(NO_2)_2(CO_2H)_2$ requires 166]. For a 1·82 per cent. solution of the sodium salt, $[\alpha]_D = +225{\cdot}3°$.

Brucine 1-γ-6 : 6′-*dinitrodiphenate*,

$$C_{12}H_6(NO_2)_2(CO_2H)_2,2C_{23}H_{26}O_4N_2,4H_2O,$$

melts and decomposes at 207—208°; for the anhydrous salt, $[\alpha]_D = -43{\cdot}67°$ in 1·44 per cent. chloroform solution. For an entirely different sample, $[\alpha]_D = -42{\cdot}98°$ in 1·46 per cent. chloroform solution. One part dissolves in approximately 95 c.c. of boiling water. Analyses were made both of the hydrated salt (Found: N = 7·15; H_2O = 6·04. $C_{60}H_{60}O_{16}N_6,4H_2O$ requires N = 7·05; H_2O = 6·11 per cent.) and of the anhydrous material, after drying at 120° (Found: N = 7·4. $C_{60}H_{60}O_{16}N_6$ requires N = 7·5 per cent.).

1-γ-6 : 6′-*Dinitrodiphenic Acid*, $C_{12}H_6(NO_2)_2(CO_2H)_2$.—The greater solubility of the brucine salt of this acid suggested that a better yield of the acid might be obtainable by the addition of *N*/5-ammonia solution (25 c.c.) to a solution of the salt (2·61 grams) in water (250 c.c.). In this manner, a quantity of hydrated brucine (m. p. 100—103°, and again at 176°) was precipitated, and the *l*-acid (0·36 gram) was obtained from the resulting solution by subsequent operations similar to those described for the *d*-acid. Thus obtained, it melted at 230—238°, and had an equivalent of 169·7; $[\alpha]_D = -169{\cdot}7°$ for a 0·09 per cent. solution of the sodium salt. After being kept for some time, and then recrystallised from water, the acid, which formed diamond-shaped plates, melted over a range of 230—248°, its equivalent weight was 164·4, and a 1·91 per cent. solution of the sodium salt showed $[\alpha]_D - 120{\cdot}8°$. Clearly, therefore, partial racemisation of the acid had occurred, and this probably also accounts for the discrepancies in melting point and rotatory power between the freshly isolated *d*- and *l*-acids.

4 : 6 : 4′ : 6′-*Tetranitrodiphenic Acid.*

This acid was originally prepared by Ullmann and Engi (*loc. cit.*) by the action of copper powder on methyl 2-chloro-3 : 5-dinitrobenzoate, followed by hydrolysis of the resulting methyl tetranitrodiphenate with 80 per cent. sulphuric acid. The latter operation is, however, much more satisfactorily carried out by the aid of 65

per cent. acid (45 parts), when a product, m. p. 288—289° (decomp.), is obtained [Ullmann and Engi give 284° (decomp.)]. These workers also appear to have overlooked the fact that the ester separates from hydrocarbon solvents in combination with them.

The same acid resulted when either β- or γ-6 : 6'- or 4 : 4'-dinitrodiphenic acid (2 grams) was heated for fifteen hours at 100° with nitric acid (*d* 1·51 ; 10 grams) and sulphuric acid (12 grams). The crystalline deposits were in each case filtered from the hot solutions, purified by recrystallisation from hot water, and thus obtained in flat plates, m. p. 288—289°. The products derived from each of the four sources indicated were identical, as were also the methyl and ethyl esters prepared from the silver salts.

Ethyl 4 : 6 : 4' : 6'-*tetranitrodiphenate*, $C_{12}H_4(NO_2)_4(CO_2Et)_2$, separates from benzene in colourless, almost square, rectangular plates, m. p. 103° with evolution of benzene and resolidification, refusion occurring at 125°. This is also the melting point of the colourless, elongated, hexagonal plates obtained by crystallisation of the ester from ethyl alcohol (Found: N = 12·1. $C_{18}H_{14}O_{12}N_4$ requires N = 11·71 per cent.).

Similarly, the methyl ester separates from benzene in small, pale yellow prisms, which first melt at 148°, and from xylene in large, yellow prisms, m. p. 152°, but in colourless needles, m. p. 169°, from methyl alcohol. The melting point, 176°, quoted by Ullmann and Engi could not be realised.

The Brucine Salts of 4 : 6 : 4' : 6'-*Tetranitrodiphenic Acid.*

When a solution of brucine (11·25 grams) in water was added to a hot solution of the acid (6 grams), a dark red colour was first produced, which quickly disappeared. The precipitated mixture of brucine salts was then repeatedly extracted with boiling water until the extracts no longer deposited slender, yellow needles of the more soluble salt; these were purified by repeated crystallisation from water. The residue consisted of the practically pure, less soluble salt. In this manner, 8·4 grams of the less soluble, and 6·35 grams of the more soluble, salt were obtained in a state of purity.

Brucine d-4 : 6 : 4' : 6'-*tetranitrodiphenate*,

$$C_{12}H_4(NO_2)_4(CO_2H)_2,2C_{23}H_{26}O_4N_2,$$

the less soluble of the two salts, formed yellow, five-sided plates, m. p. 252° (decomp.). One part dissolved in approximately 3500 c.c. of boiling water, and the salt was sparingly soluble in the ordinary organic solvents, but easily soluble in acetic acid. For a 1 per cent. solution in 10·4 *N*-acetic acid, $[\alpha]_D = +22·17°$ (Found: N = 9·14. $C_{60}H_{58}O_{20}N_8$ requires N = 9·25 per cent.).

Brucine l-4 : 6 : 4′ : 6′-*tetranitrodiphenate*,

$C_{12}H_4(NO_2)_4(CO_2H)_2,2C_{23}H_{26}O_4N_2,2\frac{1}{2}H_2O$,

m. p. 196—197° (decomp.), dissolves in approximately 1500 c.c. of boiling water, and for a 1 per cent. solution in 10·4 *N*-acetic acid $[\alpha]_D = -39·37°$ (Found: $H_2O = 7·05$. $C_{60}H_{58}O_{20}N_8,2\frac{1}{2}H_2O$ requires $H_2O = 6·92$ per cent. Found: for the anhydrous salt, N = 9·14. $C_{60}H_{58}O_{20}N_8$ requires N = 9·25 per cent.).

l-4 : 6 : 4′ : 6′-*Tetranitrodiphenic Acid.*

A boiling solution of the racemic acid (2·74 grams) in water (4500 c.c.) was gradually treated with brucine (2·56 grams), and finally filtered from precipitated brucine *d*-4 : 6 : 4′ : 6′-tetranitrodiphenate [0·1 gram, m. p. 252° (decomp.)]. More of the same salt [1·6 gram, m. p. 244—245° (decomp.)] separated on cooling. By concentration to 1000 c.c., a mixture of salts [1·7 gram, m. p. 195—196° (decomp.)] was obtained. Similar material [0·25 gram, m. p. 196° (decomp.)] was obtained by further concentration to 300 c.c. On evaporation to 120 c.c., a separation of acid was obtained, which was washed with dilute sulphuric acid until the washings gave no coloration with nitric acid, and subsequently with water. The material thus obtained (0·2 gram) melted at 281—282°, and had an equivalent of 210·3 [$C_{12}H_4(NO_2)_4(CO_2H)_2$ requires equivalent = 211]. For the 1 per cent. solution of the sodium salt, obtained from this determination, $[\alpha]_D = -19·28°$, but after some days the rotatory power was zero. In view of this observation, and those made with *l*-γ-6 : 6′-dinitrodiphenic acid it seems very probable that partial racemisation may have occurred during the operations leading to the isolation of the active acid in the present case.

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LXXII.—*Studies of the Constitution of Soap Solutions. Solutions of Sodium Palmitate, and the Effect of Excess of Palmitic Acid or Sodium Hydroxide.**

By James William McBain, Millicent Taylor, and Mary Evelyn Laing.

Both the nature and extent of hydrolysis of soap solutions have long been in dispute. In previous communications it has been shown by several methods that the actual hydrolysis is only slight, whilst the data in the present paper indicate that an acid soap, of fairly definite composition, is produced.

It will be shown that on the addition of palmitic acid to solutions of sodium palmitate at 90° both conductivity and osmotic activity nearly disappear when one equivalent of acid is present to two equivalents of palmitate, corresponding with the formation of an insoluble, colloidal acid soap † of this composition. It therefore follows that in all but the most dilute soap solutions the equation of hydrolysis must be written :

$$3NaP + H_2O = HP,2NaP + NaOH. \quad . \quad . \quad . \quad (1.)$$

A method has been developed for ascertaining within narrow limits the concentrations of the various constituents of soap solutions by utilising the data of the measurements of conductivity and osmotic pressure. Other measurements recorded in this paper afford data towards the solution of the difficult problem as to the effects of added electrolytes on the constitution and properties of soap solutions.

Density of Solutions.

Throughout this work the purest materials (Kahlbaum) were used, and the methods were the most accurate which have been

* *Ber.*, 1910, **43**, 321; *Z. physikal. Chem.*, 1911, **76**, 2; T., 1912, **101**, 2042; *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Z.*, 1913, **12**, 256; T., 1914, **105**, 957; *J. Soc. Chem. Ind.*, 1918, **37**, 249T; *Proc. Roy. Soc.*, 1920, [*A*], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426; T., 1919, **115**, 1279; 1920, **117**, 530.

† Several investigators have recently had difficulty in understanding what is commonly referred to by most authors as acid soap (for instance, M. H. Fischer, " Soaps and Proteins," 1921, p. 110), since the acid is only monobasic. The acid soaps are formulated in analogy with the well-known crystalline salts : $C_2H_3O_2K + C_2H_4O_2$ and $C_2H_3O_2K + 2C_2H_4O_2$. Evidence of the existence of acid soaps lies not so much in the analysis of sediments or materials which may not be homogeneous as in the results of such phase-rule investigations as that of Donnan and White and the evidence submitted in the present paper.

devised in this laboratory. Although no new difficulties were encountered in the alkaline and less acid solutions, strong solutions of the acid soap corresponding with HP,2NaP constituted viscous masses, which retained air bubbles most tenaciously and frothed very readily. Both time and trouble were devoted to ensuring that the results, although not very accurate, were yet essentially trustworthy.

The pyknometer employed was that described by Cornish, the results being reproducible to four significant figures (*Z. physikal. Chem.*, 1911, **76**, 210). In the case of all the extreme acid soaps, the pyknometer was filled at 90°, cooled to break air bubbles, and filled up again four or five times until no further increase in weight could be obtained. In every case the density of solutions containing acid soap is less than that of water, although a sediment of this material is denser than water. The same remarkable result had already been obtained in the case of neutral soap solutions.

Conductivity.

These measurements were carried out and corrected in the same careful manner as the previous conductivity measurements (*Z. physikal. Chem.*, 1911, **76**, 179). In the special case of the 0·4*N*-solution of HP,2NaP, which consisted of large lumps of transparent jelly containing air spaces, it was considered better to use the low density value observed for the calculation of the molecular conductivity rather than to employ the undoubtedly more accurate value which could be obtained by extrapolation. Throughout this paper concentrations are expressed in weight normality, being gram-equivalents per 1000 grams of water.

TABLE I.

Conductivity at 90·00° of Solutions of Sodium Palmitate containing 25 per cent. or 50 per ceut. excess of Palmitic Acid.

Na.	HP.	κ.	$D_{4°}^{90°}$.	μ.	Mean.
0·400*N*	0·500*N*	0·01496	0·9626	44·3	44·0
,,	,,	0·01474	,,	43·6	
0·201*N*	0·251*N*	0·008848	0·9634	48·9	54·0
,,	,,	0·0107	,,	59·2	
0·400*N*	0·600*N*	0·00256 *	0·8634	8·85	8·85
0·200*N*	0·300*N*	0·00183 *	0·9610	10·3	12·7
,,	,,	0·00205 *	,,	11·6	
,,	0·301*N*	0·00289 *	,,	16·2	
0·101*N*	0·153*N*	0·00251 *	0·9638	26·9	25·4
,,	0·152*N*	0·00224 *	,,	24·0	

* Mean specific conductivity = 0·00235.

Note.—These colloidal sols of HP,2NaP were not fully homogeneous.

The conductivities of solutions of sodium palmitate containing excess of palmitic acid or of sodium hydroxide are collected in Table II, which thus presents the whole range of molar conductivity from acid sodium palmitate to pure sodium hydroxide. The molar conductivity μ given in the third column is based on the total concentration of the sodium in the solution. Values are given in the fourth column for μ_∞, which is taken, in accordance with previous papers, as 550 for sodium hydroxide, 229 for sodium palmitate and for $NaHP_2$, whilst for intermediate mixtures it is interpolated in the manner explained below. The fifth column contains the apparent degree of dissociation, $\alpha = \mu/\mu_\infty$; the sixth the total concentration of sodium ions deduced by multiplying the total concentration of sodium by α. In the case of the acid sodium salts, even where the specific conductivity is independent of the concentration, the molar conductivity is arbitrarily taken as the specific conductivity multiplied by the total volume of the mixture; and no corrections have been applied to the values in these special cases.

TABLE II.

Conductivity and Apparent Ionisation of Solutions at 90° containing Various Proportions of Palmitic Acid and Sodium Hydroxide.

Conc. of NaP.	Conc. excess.	μ	μ_∞	α per cent.	Conc. of Na˙.
1·0*N*	1·0*N*-NaOH	176	440·5	40·0	0·800
0·8*N*	0·8*N*-HP	1·3	229	0·6	0·004
0·4*N*	0·4*N*-HP	2·5	,,	1·1	0·004
,,	0·2*N*-HP	8·9	,,	3·9	0·010
,,	0·1*N*-HP	44·0	,,	18·0	0·072
,,	0·4*N*-NaOH	230	446·1	51·56	0·413
0·2*N*	0·2*N*-HP	5·0	229	22·0	0·004
,,	0·1*N*-HP	12·7	,,	5·6	0·010
,,	0·05*N*-HP	54·1	,,	23·5	0·044
,,	0·2*N*-NaOH	245	452·9	54·11	0·216
,,	0·6*N*-NaOH	317	335	62·37	0·501
0·1*N*	0·1*N*-HP	10	229	4·4	0·004
,,	0·05*N*-HP	25·4	,,	11·1	0·010
,,	0·1*N*-NaOH	258	456·3	56·54	0·113
,,	0·3*N*-NaOH	340	451·2	75·36	0·301

*Osmotic Activity.**

The osmotic behaviour of the soap solutions containing excess of hydroxide or of acid was studied by determining the lowering of vapour pressure or rise of boiling point by means of the dew-point method already described (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 45; *J. Amer. Chem. Soc.*, 1920, **42**, 428), which is the

* Experiments by M. E. L.

only known method which is applicable to some of the cases here investigated. It is accurate, as here applied, to 0·01°. It possesses the great advantage that its accuracy is quite independent of the physical state of the material undergoing investigation, whether this is a solid, a liquid, or a paste. The dew-point lowering is proportional to the concentration of crystalloidal matter present, and at 90° it amounts to 0·483° for 1·0*N*-crystalloid.

The results are collected in Table III. The next to the last column gives total concentrations of crystalloid, which includes sodium ion, hydroxyl ion if any, simple palmitate ion, and simple undissociated sodium hydroxide. The last column is an indication of the degree of osmotic activity, van't Hoff's *i* value being the ratio of the osmotic activity actually exhibited to that predicted for any crystalloid, such as urea, in a solution of the same concentration as the total amount of sodium present.

TABLE III.

Dew-point Lowering and Osmotic Activity of "Solutions" at 90° containing Various Proportions of Sodium Hydroxide and Palmitic Acid.

Conc. of NaP.	Conc. excess.	Dew-pt. lowering.	Conc. of crystalloid.	Van't Hoff's *i* value.
1·00*N*	0·25*N*-NaOH	0·42°	0·87*N*	0·70
,,	0·50*N*-NaOH	0·59	1·22*N*	0·81
,,	1·00*N*-NaOH	0·93	1·93*N*	0·96
0·80*N*	0·80*N*-HP	0·01	0·02*N*	0·02
0·40N	0·40*N*-HP	0·00	0·00*N*	0·00
,,	0·20*N*-HP	0·005	0·01*N*	0·02
,,	0·10*N*-HP	0·12	0·25*N*	0·03
,,	0·40*N*-NaOH	0·44	0·91*N*	1·14
,,	1·00*N*-NaOH	0·76	1·64*N*	1·17
0·20*N*	0·20*N*-HP	0·01	0·02*N*	0·10
,,	0·10*N*-HP	0·005	0·01*N*	0·05
,,	0·05*N*-HP	0·06	0·12*N*	0·60
,,	0·20*N*-NaOH	0·24	0·50*N*	1·25
,,	0·60*N*-NaOH	0·51	1·08*N*	1·35
,,	1·00*N*-NaOH	0·80	1·66*N*	1·38
0·10*N*	0·10*N*-HP	0·00	0·00*N*	0·00
,,	0·05*N*-HP	0·005	0·01*N*	0·10
0·04*N*	0·04*N*-HP	0·00	0·00*N*	0·00

General Trend of the Results and Nature of the Products of Hydrolysis of Soap.

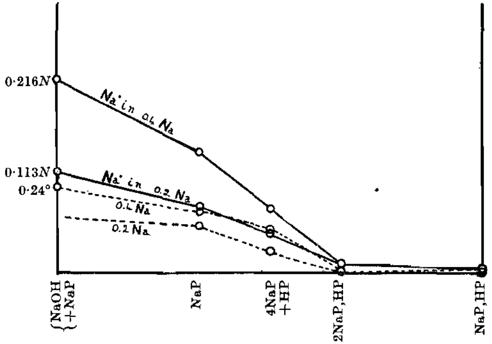
The conductivity of a solution of sodium hydroxide, to which increasing amounts of palmitic acid are added, diminishes almost linearly with such additions until the composition, sodium palmitate (NaP), is attained. At this point there is a break, and with increas-

ing excess of palmitic acid the conductivity again falls linearly until a very low value is attained at the composition 2NaP,HP. From this point onwards the further decrease of conductivity is relatively unimportant.

Similarly, in Fig. 1, the values given in Table II for the concentration of sodium ion are plotted against increasing amounts of palmitic acid added to sodium hydroxide. Here again, the concentration of sodium ion is seen to fall steadily until the composition NaP is reached, then further, to a value of about 0·10*N* at the com-

FIG. 1.

Effect of addition of palmitic acid on dew-point lowering and concentration of sodium ion in solutions containing 0·4N- *or* 0·2N- *content of total sodium.* (*Broken lines represent dew-point lowering.*)



position 2NaP,HP, and thence to 0·004*N* at the composition NaP,HP.

The last two values are independent of the absolute concentration of the solution and depend only on the ratio of sodium and palmitic acid. This would be the behaviour expected in the case of a slightly soluble solid of a composition 2NaP,HP, the limiting member of a series of solid solutions ranging in composition from 2NaP,HP to NaP,HP or beyond.

In Fig. 1 the dew-point lowering as shown in Table III is also plotted on the same co-ordinates. These osmotic data are very similar to the conductivity results just described. The concentration of crystalloid present falls steadily as the sodium hydroxide

is converted to sodium palmitate; crystalloidal matter has almost disappeared from solution when the composition, acid soap, 2NaP,HP, is attained. This again shows that solids of composition between 2NaP,HP and NaP,HP are only slightly soluble.

It is evident that a relatively insoluble " acid soap " of approximate composition 2NaP,HP, whether a solid solution or not, is to be regarded as the product of hydrolysis in soap solutions at 90° (equation 1).

Previous communications have established that such products must be acid soap and not free fatty acid, since palmitic acid is not much weaker than acetic acid, and free acid cannot exist in appreciable amounts in presence of the concentration of hydroxyl ion (0·001*N*) actually observed in aqueous solutions of sodium palmitate. We have found that even as little as 0·00003*N*-free OH′ corresponds with the formation of acid soap of the composition NaP,HP, and only 0·0002*N*-OH′ completes the formation of the most nearly neutral of these acid soaps, 2NaP,HP; in other words, this limiting member of the acid soaps is formed in the presence of alkali which is only one-fifth of that subsisting in ordinary soap solutions. Further increase of alkali would therefore merely diminish the amount of this limiting member of the series of acid soaps.

Krafft and his co-workers (*Ber.*, 1894, **27**, 1747, 1755; 1895, **28**, 2566, 2573), and likewise Arndt and Schiff (*Koll. Chem. Beihefte*, 1914, **6**, 201), analysed the sediment obtained from very dilute solutions of sodium palmitate at the ordinary temperature and found that this consisted of acid soap, which, in extreme dilution, corresponded approximately with the formula NaP,HP. In somewhat less dilute solutions, however, the sediment approached more nearly to the composition of neutral soap. We know now that no stress can be laid on definite values obtained in this way owing to the very slight solubility of sodium palmitate itself. This source of error can be avoided by slightly raising the temperature. Reychler (*16th Vlaamsch Natuur-en Geneeskundig Congres*, Leuven, 1912, 69; *Eighth Inter. Congress Applied Chem.*, 1912, **22**, 221) carried out experiments which were subject to the same error, but showed, within certain limits of dilution, that the conductivity of the mother-liquor was sensibly constant. Zsigmondy and Bachmann (*Z. Chem. Ind. Kolloide*, 1913, **11**, 145) isolated traces of sediment from potassium palmitate and potassium stearate solutions at 60° and found that they melted 100° below the melting point of the pure neutral soaps, from which they concluded that they were acid soaps; part of the effect was possibly due to hydration.

A careful study was made by Donnan and White (T., 1911, **99**,

1667) of mixtures of anhydrous sodium palmitate and palmitic acid, which, however, always contained much more palmitic acid than corresponded with the formula NaP,HP. They proved that two series of solid solutions of acid soap are formed, with a transition point at 70°, which, curiously enough, they misinterpreted as a eutectic point. The solid solutions they actually investigated contained from 10 per cent. to 40 per cent. of sodium palmitate, so that the compound which forms the basis of this solid solution of palmitic acid must contain still more sodium palmitate and may well be NaP,HP; it is further probable that this series of solid solutions of acid soap is continued as far as the limit which we have found, 2NaP,HP.

What we have not done in the present paper is to inquire concerning *a shift of this limit of 2NaP,HP towards NaP,HP as the* temperature is altered. Further, it remains to be seen as to whether *the composition of the acid soap is not different in the case of the* salts of the other fatty acids.

In any case, the acid soaps formed as a result of hydrolysis appear to be colloidal in nature, as is evident from the description of the solutions given in this paper. Further, it is probable that they are quite appreciably hydrated. Hence, even in extreme dilution, where the soap itself is largely in the form of an ordinary simple electrolyte, there is still an appreciable amount of colloidal matter. On cooling the stronger solutions, a silky, fibrous curd of acid soap is obtained, whereas in more dilute solutions an apparently microcrystalline sediment appears.

The Constituents of Solutions of Sodium Palmitate at 90°.

Previous communications have shown that it is possible to determine the nature and amount of the various constituents in soap solutions by comparison of conductivity and osmotic activity (McBain and Salmon, *Proc. Roy. Soc.*, 1920, [*A*], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426; McBain, Laing, and Titley, T., 1919, **115**, 1279). In this way the existence of the ionic micelle and its high mobility in concentrated solutions were established.

It was, however, possible to determine the relative concentrations of the various constituents in some of the solutions merely from this direct comparison only within certain limits. We now point out that the concentrations of all constituents become defined within the experimental error, if the usual formula is applied to the equilibrium which must exist between the simple crystalloidal sodium palmitate present and the sodium and simple palmitate ions.

Many investigators have shown that the dissociation of strong

electrolytes is in accordance with an empirical formula of the form :

$$\frac{\alpha^n}{(1-\alpha)\ V^{(n-1)}} = K,$$

where n varies between the limits 1·40 and 1·55, but is usually nearly 1·50. It has been shown that this formula may be extended to solutions containing mixtures of any electrolytes with or without a common ion (Sherrill, *J. Amer. Chem. Soc.*, 1910, **32**, 741; Bray and Hunt, *ibid.*, 1911, **33**, 781, etc.).

In the present case, a solution of sodium palmitate is to be regarded as a mixture of simple electrolyte, NaP, and colloidal electrolyte, with the sodium ion in common. The following formula will therefore give, very closely, the necessary relationship between the concentration of the three chief crystalloidal constituents of sodium palmitate solution, the value of the constant being determined from the existing data for 0·1N-solution :

$$\frac{[Na^{\cdot}]^{0 \cdot 5}[P']}{[NaP]} = K = 0 \cdot 104.$$

It is now possible to recalculate more closely our previously published results. This is done by following the methods already described, taking the mobility of the sodium ion as 139, of the palmitate ion as 90, and of the ionic micelle as 139, calculating the concentrations from the conductivity accordingly, and ascertaining by trial the only values for these concentrations which would satisfy the formula just given.

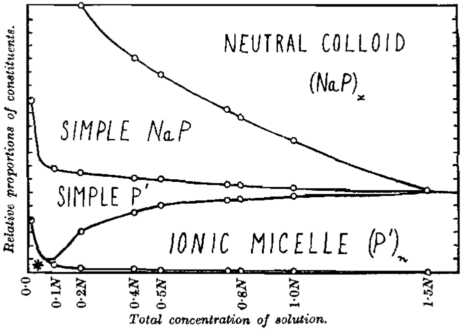
The results for sodium palmitate are given in Fig. 2, in which the percentage amount of each constituent present is plotted against the total concentration of the solution (the lowering of dew-point for 0·2N-sodium palmitate is taken as 0·12° instead of 0·13° as given by McBain and Salmon). These individual percentages must add up to 100 for each solution, so the whole diagram is subdivided into fields representing the proportionate amount of each of the five main constituents for each soap solution between 0·1N and 1·5N. The amount of acid soap is known from our previous measurements of the alkalinity of soap solutions, some of which have been published; and the first section of this paper enables us to calculate the proportion of palmitate thus accounted for as acid soap. The remaining constituents are, ionic micelle, simple palmitate ion, these two together being of course equal in amount to the sodium ion; and lastly the simple crystalloidal sodium palmitate and the neutral colloidal sodium palmitate. As in McBain and Salmon's paper, the ionic micelle has been calculated as pure, agglomerated palmitate ion, $(P')_n$. Thus the whole of the colloidal $(NaP)_m$ is reckoned as "neutral colloid," although it is

certain that part of it is sorbed by the ionic micelle, and only part exists independently.

It will be noted that the neutral colloid first appears in appreciable quantity in solutions which are above 0·2*N*, whilst in concentrated solutions the bulk of the soap is in this form. No matter how the data for 0·2*N*-sodium palmitate are calculated, using varying sets of assumptions, and making allowances for possible experimental error, they suffice to show that the amount of neutral colloid present is inappreciable, whereas the amount of the ionic

FIG. 2.

*The relative proportions of the various constituents of solutions of pure sodium palmitate at 90°. (The asterisk * marks the field showing the proportion of acid soap, 2NaP,HP, present.)*



Total concentration of solution.

micelle must be about one-third of that of the sodium ion. These conclusions are only emphasised if the mobility of the ionic micelle is assumed to be as low as that of the palmitate ion.

In more dilute solution the ionic micelle itself disappears, whereas, through hydrolysis, the amount of acid soap, which is itself a colloid, becomes relatively much greater,* and the dissociation of the

* Iredale (T., 1921, **119**, 625) has criticised our view that soap itself does not exist in colloidal form in dilute solution on the ground that dilute solutions still exert a protective action on gold and silver sols. This protective action must be due to the colloidal acid soap produced by hydrolysis, since, as yet unpublished experiments show, certain foams contain acid soap. The results in the present paper serve merely to fortify the statement made by McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179) that the acid soaps are typically colloidal.

simple sodium palmitate, like that of any other simple electrolyte, tends towards completion at infinite dilution.

It is very noticeable that the dissociation of the colloidal electrolyte into sodium ion and ionic micelle follows no such law as that of an ordinary electrolyte. In fact, the proportion of sodium ions preseut is only slightly diminished in passing from $0{\cdot}2N$ to $1{\cdot}5N$, in spite of the enormous alteration in the concentration of neutral colloid and the amount of ionic micelle relative to it. Suggestions to account for this have already been given in the alteration in composition and hydration of the ionic micelle, with change in concentration. It is now even more evident that the proportion of neutral colloid contained in the ionic micelle can be large only in concentrated solutions.

It is important to note, in view of the discussion of the effect of added electrolyte (see below), that the amounts of crystalloidal and colloidal constituents in pure sodium palmitate solutions are calculated solely from the conductivity and osmotic data, the equation we have introduced being used merely to condition the allotment of the available crystalloidal material. Bearing in mind the degree of accuracy, experimental and theoretical, to be expected in the interpretation of the results of conductivity and osmotic measurements, it appears likely that we have determined the various constituents to within about 10 per cent. of the total concentration of the solution.

Solutions containing Excess of Palmitic Acid.

The methods of the foregoing section are readily applied to the calculation of the data of solutions containing excess of palmitic acid. This has been done for the two cases in which a 25 per cent. excess of palmitic acid has been added to $0{\cdot}4N$- and $0{\cdot}2N$-solutions of sodium palmitate. It will be noted that the composition of the palmitate in these solutions lies half-way between that of sodium palmitate (NaP) and the acid soaps (2NaP,HP). It follows therefore that we are here dealing essentially with solutions in which half of the palmitate has been removed, for practical purposes, as indifferent colloidal material, part of which often segregated out. Hence the concentrations of the constituents present in these solutions should be those of $0{\cdot}2N$- and $0{\cdot}1N$-sodium palmitate respectively. This comparison is effected in Table IV, and it will be seen that the results afford satisfactory confirmation of these views. It should be remembered that the dew-point measurements did not measure concentrations more closely than to $0{\cdot}02N$.

TABLE IV.

Comparison of the Concentrations of the Constituents of Solutions of Sodium Palmitate at 90° with and without excess of Palmitic Acid.

	$Na^{\cdot}$.	P′.	$(P')_n$.	NaP.	$(NaP)_x$.
0·2*N*-NaP	0·074	0·05	0·03	0·13	0·00
0·4*N*-NaP + 0·1*N*-HP	0·072	0·05	0·02	0·13	0·00
0·1*N*-NaP	0·035	0·03	0·00	0·06	0·00
0·2*N*-NaP + 0·05*N*-HP	0·044	0·03	0·01	0·06	0·00

Study of the separate constituents of solutions containing 50 per cent. or 100 per cent. excess of palmitic acid lies beyond the range of accuracy of the osmotic method here employed; thus, although there are hints that the ionic micelle tends to persist in greater dilution in the presence of, or possibly when stablised by, acid soap, no stress can be laid upon the data.

Solutions of Sodium Palmitate containing Excess of Sodium Hydroxide.

Much greater difficulty attaches to the detailed calculation of the alkaline solutions. It is necessary to introduce some further relation such as the formula :

$$\frac{[Na^{\cdot}]^{0 \cdot 5}[OH']}{[NaOH]} = K = 2{\cdot}13.$$

However, examination of the data for solutions containing the highest concentrations of sodium hydroxide shows that no matter how the concentrations are allotted, this formula, which undoubtedly governs the true dissociation of the sodium hydroxide, is not satisfied.

In more extreme cases, it would be necessary not only to assume relatively large amounts of crystalloidal soap, but also to suppose that an appreciable fraction of the sodium hydroxide has been removed from solution by sorption hy the soap. The first part of this suggestion is directly negatived by the results of several methods not yet published (ultra-filtration and *E.M.F.*); the second part we should be loth to accept in view of the pronounced negative sorption of solutions of sodium hydroxide in the presence of salted-out soap (McBain and Taylor, T., 1919, **115**, 1300, etc.).

The most interesting case is certainly the solution which is normal both with regard to sodium hydroxide and sodium palmitate. Here the conductivity observed (176) is less than the conductivity of a normal solution of sodium hydroxide alone. Similar cases have been observed by Kurzmann (*Diss.*, Karlsruhe, 1914; *Koll. Chem. Beihefte*, 1914, **51**, 427), namely, potassium hydroxide or potassium carbonate in the presence of the soap of palm-kernel

oil at 90° as well as at 20°. Ten years ago, in the total absence of trustworthy osmotic data, it seemed permissible to suggest that this might be due to driving back of hydrolysis of soap solution; this view would now be quite untenable.

The most probable suggestion is that the dissociation of the soap is well driven back, so that crystalloidal material has practically disappeared, although dissociation of the colloid as ionic micelle may still be appreciable. The solution is thus filled with a high concentration of neutral colloid, whose bulk may be inferred from the fact that only 1000 grams of water are contained in 1310 c.c. of solution. This large volume of colloidal matter must present serious obstruction to electrical conduction through the solution. Measurements of this effect will be published later. A second influence arises from the hydration of this soap, which enhances, in the well-known fashion, the apparent osmotic activity and hence the concentration of crystalloidal matter. A rough calculation shows that these effects are sufficient to account for the data observed.

The data in Table II were tentatively calculated as though in the mixture the mutual influence of soap and hydroxide on each other's dissociation was in proportion to their dissociation when taken separately. The results of calculation on this basis would indicate that the dissociation of the soap is even less than that of a pure soap solution of the same total concentration, but that the type of dissociation is altered in much the same fashion as in Fig. 2. Hence the effect of addition of an electrolyte to even a dilute soap solution is to produce, almost immediately, a high proportion of colloid.

We have further measured by means of the hydrogen electrode the concentration of the hydroxyl ion in the solution containing $1{\cdot}0N$-sodium palmitate and $1{\cdot}0N$-sodium chloride. C. S. Salmon has measured for us the concentration of sodium ion with a sodium electrode. After calculating the diffusion potential, he has deduced the following values for the concentrations of the conducting constituents: $Na^{\cdot}=0{\cdot}75N$, $OH'=0{\cdot}43N$, whence $(P')_n=0{\cdot}32N$. These values, although inaccurate, are in general agreement with those used in Table II as calculated from conductivity and osmotic activity; namely, $Na^{\cdot}=0{\cdot}80N$, $OH'=0{\cdot}57N$, $(P')_n=0{\cdot}23N$. Both sets of data indicate that dissociation of soap into ionic micelle is still very appreciable in spite of the large amount of added electrolyte.

Summary.

1. Conductivity and dew-point have been determined for solutions of sodium palmitate containing excess or deficit of palmitic acid.

2. Osmotic activity and specific conductivity are rapidly diminished by excess of palmitic acid, having nearly disappeared when the proportion of palmitate to sodium is as five to four.

3. It is shown that colloidal acid soaps, and not free palmitic acid, are the products of hydrolysis of sodium palmitate. The composition of the most nearly neutral of the series corresponds with the empirical formula 2NaP,HP, ranging down to NaP,HP and beyond.

4. A means has been found of calculating more closely from conductivity and osmotic activity the concentration of each of the constituents present in soap solutions at various concentrations.

5. Addition of an electrolyte such as sodium hydroxide rapidly increases the amount of neutral colloid and almost eliminates crystalloidal soap, whilst still leaving an appreciable proportion of ionic micelle.

In conclusion, we desire to express our thanks to the Colston University Research Society of the University of Bristol and to the Research Fund of the Chemical Society for grants towards the purchase of materials and apparatus.

DEPARTMENT OF PHYSICAL CHEMISTRY,
THE UNIVERSITY, BRISTOL. [*Received, February 3rd*, 1922.]

LXXIII.—*New Halogen Derivatives of Camphor. Part II. α′-Bromocamphor.*

By THOMAS MARTIN LOWRY, VICTOR STEELE, and HENRY BURGESS.

THE existence of two stereoisomeric bromocamphors, as products of bromination of camphor, was discovered in 1890 by Marsh (T., 1890, **57**, 828; 1891, **59**, 968), who showed that the crude α′-bromocamphor could be converted into α-bromocamphor by distillation under atmospheric pressure. As long ago as 1878 Armstrong (*Chem. News*, 1878, **37**, 4) had shown that alcoholic potassium hydroxide could be used to convert the crude product of bromination into α-bromocamphor in almost quantitative yield; but it was not until 1905 that Kipping (P., 1905, **21**, 125) made the important discovery that the isomeric change of the stereoisomeric bromocamphors in presence of alcoholic potash is reversible, but can be suspended by the addition of acids. By making use of this fact, he was able to reduce the rotatory power of bromocamphor from $[\alpha]_D + 135°$ to $+ 38{\cdot}5°$ by partial conversion of the α- into the α′-form. Measurements of the solubility of α-bromo-

camphor in alcohol, with and without an alkali (Lowry, T., 1906, **89**, 1033), showed that the solubility increased in the ratio of 0·905 to 1, but that the rotatory power of the saturated solution remained almost constant, increasing only from 40·5° to 40·8° in 98·7 per cent. alcohol and from 41·0° to 41·6° in 99·5 per cent. alcohol. These observations indicated that the less stable isomeride was of very low rotatory power, and indeed almost inactive; but, since the solubility of α-bromocamphor in alcohol is almost certainly increased by the presence of the α′-isomeride, it was suggested that the rotatory power of the latter must be negative in order to account for the almost constant rotatory power of the saturated solution.

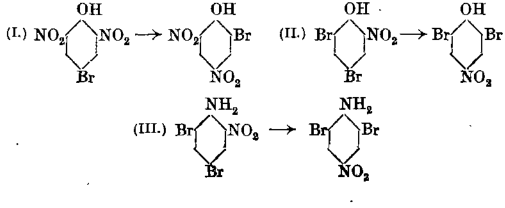
In the present series of experiments we have made use of Kipping's method in order to prepare from pure α-bromocamphor a mixture of the two stereoisomerides. The separation of these is much more difficult than in the case of the chlorocamphors, on account of the lower melting point and greater solubility of the compounds, mixtures of which tend to solidify in a glassy form, or to separate as oils when a solvent is present. We have, however, been able to carry the fractionation of the mixture to a point at which the α′-bromocamphor was obtained with a constant melting point and rotatory power. The final product crystallised from alcohol in needle-shaped crystals, and by slower crystallisation gave well-developed crystals, which could be measured on the goniometer, and were obviously free from all but isomorphous impurities. It is of interest to note that the pure material is strongly lævorotatory, giving $[\alpha]_{5461}$ − 40° as compared with $[\alpha]_D$ + 38·5° and + 29·4°, the lowest values recorded by Kipping and by Marsh for mixtures rich in the α′-compound. The rotatory power of α-bromocamphor under these conditions (10 grams per 100 c.c. of alcoholic solution at 20°) is + 165°, a difference of more than 200° as between the two isomerides; but on the addition of a small amount of alkali the rotations of both isomerides change to the same final value, $[\alpha]_{5461}$ + 149°.

From these rotations it appears that the proportion of α-bromocamphor in the equilibrium mixture is 92 per cent. Measurements of solubility gave an uncorrected ratio of 90 per cent., but this was raised to 93 per cent. when a correction was made for the influence of α′-bromocamphor on the solubility of α-bromocamphor, on the assumption that the α′-compound would have the same effect as an equal weight of β-bromocamphor in increasing the solubility of the main constituent. The two determinations of the proportions of the isomerides when in equilibrium with one another therefore agree within 1 per cent.—an agreement which is remark-

ably close, in view of the difference in the methods used for the two determinations.

In the previous paper of this series it was stated that when α- and α′-chlorocamphor are brominated, they yield an identical mixture of the isomorphous αα′- and α′α-chlorobromocamphors. Since the isomorphous mixture has exactly the same rotatory power, and therefore exactly the same composition, in both cases, it is almost certain that it is an enolic form of the chlorocamphors that is brominated and not the ketones themselves. We have attempted to repeat this experiment with the two bromocamphors; but whilst α-bromocamphor can be chlorinated readily by means of sulphuryl chloride, α′-bromocamphor has given only oily products in a series of seven experiments, and we did not think it worth while to sacrifice more material in order to obtain proof of the almost obvious fact that chlorination, as well as bromination, takes place by means of an attack on an enolic form.

A much more important point of contrast is found on comparing the behaviour towards nitric acid of the bromo- and chloro-camphors. In the case of the chlorocamphors, each compound yielded its own nitro-derivative, and there was no indication of any shifting of the halogen atom during nitration. Much to our surprise, however, we found (and confirmed by repeated experiments) that both bromocamphors give the same nitro-derivative, namely, the common αα′-bromonitrocamphor, in which the bromine occupies the α-position and the nitro-group the α′-position, rendering the compound lævorotatory, although the stereoisomeric α′α-bromonitrocamphor is dextrorotatory. We are not able to offer any explanation of this curious difference between the two halogens; but there are on record observations on derivatives of benzene which are almost identical with the facts which we have observed in the camphor series and which show that bromine may become mobile under conditions which leave a chlorine atom completely stable. Thus, Armstrong observed in 1875 (T., 1875, **13**, 520) that under the influence of bromine, 4-bromo-2 : 6-dinitrophenol (I) and 2 : 4-



dibromo-6-nitrophenol (II) undergo an isomeric change, in which a nitro-group wanders from the *o*- to the *p*-position and a bromine atom from the *p*- to the *o*-position. The same change takes place when 4 : 6-dibromo-2-nitroaniline (III) is acted on by concentrated hydrochloric or sulphuric acid (Orton and Pearson, T., 1908, **93**, 725), but the change does not take place in the corresponding chlorine compounds, and is also stopped when the hydrogen of the hydroxyl group is replaced by an alkyl group.

Experimental.

Preparation.—The material used in these experiments was prepared, in the same way as in the case of α′-chlorocamphor (Lowry and Steele, T., 1915, **107**, 1382), by dissolving α-bromocamphor in boiling alcohol, adding sodium ethoxide in order to produce a condition of dynamic isomerism, and then acidifying with hydrochloric acid to render the isomerism static. Most of the α-bromocamphor was separated from the alcoholic solution by freezing, and used again; but the removal of the parent substance was much less complete than in the case of α-chlorocamphor. Thus, the lowest readings obtained from the mother-liquors, even after six crystallisations, gave specific rotations of about + 24° for light of wave-length 5461. This appears indeed to be approximately the rotatory power of a mixture of the two isomerides when they saturate simultaneously an alcoholic solution. It may be noted that three such mixtures, which had been melted and poured into distilling flasks, with the view of attempting the separation of the isomerides by fractional distillation, remained in an amorphous condition as a yellow resin or glass for six years, from 1915 to 1921, without showing any sign of crystallisation. This recalls Marsh's description of mixtures of similar rotatory power as "yellowish, soft, and of a camphorous consistency."

Fractionation.—The fractions described above were distilled in the vacuum of a Langmuir mercury-vapour pump under a pressure of 1·12 mm., which is apparently the vapour pressure of the glassy mixture of isomerides at 0° to 5°. No important separation was effected, as is shown by the following figures :—

Before distillation . .	$[\alpha]_{5461} = +27{\cdot}2°$
1st fraction . . .	$[\alpha]_{5461} = +31{\cdot}2°$
2nd ,, . . .	$[\alpha]_{5461} = +30{\cdot}8°$
3rd ,, . . .	$[\alpha]_{5461} = +31{\cdot}6°$

The distillation served, however, to remove any impurities that had accumulated up to this stage of the fractionation, and to convert the yellow resin into a perfectly colourless, camphor-like mass.

A number of trials were made in order to see if solvents with a different ratio of solubility could be used for the fractionation, but many of these, for example, acetic acid, gave oily products, and only ethyl and methyl alcohols were found to be suitable. Fractionation was finally effected by crystallising from these two solvents, and mainly from methyl alcohol cooled in a freezing mixture. Under these conditions fractions with a rotatory power of less than 20° were frequently obtained, alternating with fractions of higher rotatory power. On recrystallisation, the former gave solutions which were no longer saturated with α-bromocamphor, and therefore decreased in rotatory power, as the parent substance was left behind in the mother-liquors, until negative rotations were obtained. The last stages of purification are indicated in the following table, which gives the rotatory power and melting point as modified by successive crystallisations from alcohol, after a lævorotatory material had been produced by some four preliminary recrystallisations :

Number of crystallisations.	4	5	6	7	8	9
$[\alpha]_{5461}$ =	−12·8°	−36·1°	−37·0°	−37·8°	−39·0°	−38·6°
M. p. =	75°	76°	77°	78°	78°	78°

The rotatory powers given above are for very weak alcoholic solutions; careful determinations, using a 10 per cent. solution in ethyl alcohol in a 4-dcm. tube at 20°, gave $[\alpha]_{5461}$ − 40° as the specific rotatory power of the pure substance. The melting point at 78° was determined with a standard thermometer, in comparison with that of the α-compound, which melted 2° lower at 76°.

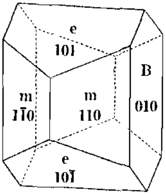
Properties.—α′-Bromocamphor is readily soluble in all organic solvents, including light petroleum and petroleum spirit. It crystallises from methyl and ethyl alcohols in needles, which become better defined as the substance becomes purer.

Measurable crystals were obtained by the slow evaporation of a solution in alcohol. These were examined, in the Mineralogical Laboratory of the University of Cambridge under the direction of Mr. A. Hutchinson, F.R.S., by Mr. E. D. Mountain of Corpus Christi College, who has supplied the following data.

System : orthorhombic, holohedral; $a : b : c = 0·7389 : 1 : 0·4691$.
Forms observed : $B = \{010\}$, $m = \{110\}$, $e = \{101\}$.
Angles measured :

	No. of measurements.	Limits.	Mean.	Calc.
$m_1 : m_4 = (110) : (1\bar{1}0)$	6	72° 46′—72° 57′	72° 55′	—
$m_1 : e_1 = (110) : (101)$	6	64 28 —64 34	64 30	—
$e_1 : e_2 = (101) : (\bar{1}01)$	2	64 47 —64 57	64 49	64° 44′

Habit : short prismatic; often tabular parallel to *m*(110); more rarely tabular parallel to *e*(101).



Cleavage : none observed.

Density : by weighing in a solution of potassium mercuri-iodide at 14° = 1·484.

Topic axial ratios : $\chi = 5{\cdot}658$; $\psi = 7{\cdot}658$; $\omega = 3{\cdot}592$.

The optical characters of the crystal are as follows :—

Double refraction : negative.

Optic axial plane : parallel to (001), acute bisectrix perpendicular to (100).

Refractive indices : determined by total reflexion from pinacoid face (010), the crystal being immersed in a strong solution of potassium mercuri-iodide;

$$\alpha = 1{\cdot}5535 \quad \beta = 1{\cdot}5787 \quad \gamma = 1{\cdot}5912.$$

Optic axial angle :

2V = 69° 10′ as determined in dilute potassium mercuri-iodide of approximately the mean refractive index of the crystals;

2V = 69° 16′ as calculated from refractive indices.

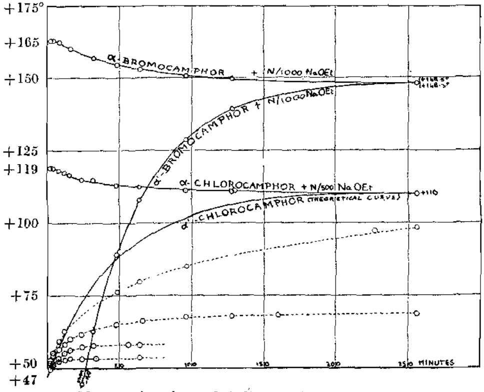
The crystalline properties of the compound are related only in a very distant way to those of the stereoisomeric α-bromocamphor, which crystallises in the monosymmetric system and only shows a slight resemblance in one zone to the α′-compound.

Although it is less stable, the density, 1·484, of α′-bromocamphor is slightly higher than that of α-bromocamphor, for which the values 1·437 and 1·449 have been recorded. The melting points of α′-bromocamphor at 78·5° and of α-bromocamphor at 76° are very close together, like those of the stereoisomeric bromonitrocamphors (Lowry, T., 1898, **73**, 987), which agree within 1°. Since no marked fractionation takes place when a mixture of the two compounds is distilled under reduced pressure, their vapour pressures must also be very similar; both compounds can be sublimed from the liquid without decomposition, although they tend to char when distilled under atmospheric pressure.

The composition of the new compound is established clearly by its preparation from α-bromocamphor and by its reconversion into this compound in presence of an alkali; it was, however, checked by an estimation of bromine (Br = 34·12, 34·40. $C_{10}H_{15}OBr$ requires Br = 34·58 per cent.).

Mutarotation.—A solution of α-bromocamphor in alcohol (5 grams in 100 c.c.) gave $[\alpha]_{5461}$ + 164·75°; but, after adding four drops of normal alcoholic potassium hydroxide to approximately 15 c.c. of the solution, the rotatory power fell to $[\alpha]_{5461}$ + 147·4°. In the case of the α'-compound the initial and final rotations under similar conditions were − 38·8° and + 147·7°, the final rotations being identical within 0·03° in the actual readings. The volume of alcoholic potassium hydroxide added to the solution was approximately 0·05 c.c., so that the final values should be corrected to

FIG. 1.



Mutarotation of α- and α'-chloro- and bromo-camphors.

+ 147·9° and + 148·2° for the two solutions. A direct determination of the final rotatory power in the presence of an alkali (added before making up to an exact volume) was $[\alpha]_{5461}$ + 149°, in good general agreement with the two approximate values recorded above. The more exact value, 149°, corresponds with the presence of 92 per cent. of α-bromocamphor in the equilibrium-mixture.

Quantitative curves for the mutarotation of α- and α'-bromocamphor and of α- and α'-chlorocamphor in alcoholic solutions in presence of sodium ethoxide are reproduced in Fig. 1. The curves for α- and α'-*bromocamphor show an equal velocity of change* towards the equilibrium-position, the mean values of the constants being $k = 0{\cdot}0210$ for α-bromocamphor and 0·0249 for α'-bromo-

camphor in presence of $N/1000$-sodium ethoxide; the corresponding "half-life periods" are thirty-three and twenty-eight minutes. In view of the minute quantity of catalyst used in both cases, the concordance is very satisfactory.

The mutarotation curve for α-chlorocamphor in presence of $N/500$-sodium ethoxide is very similar to that for the bromo-compound *at half this concentration of catalyst*, the velocity constant being $k = 0{\cdot}0218$ and the half-life period thirty-two minutes; the data are very concordant, and the curves are based on readings from three independent experiments. The mutarotation curves for α′-chlorocamphor are, however, abnormal. A theoretical curve, using the same velocity constant and half-life period as for α-chlorocamphor, is shown by a full line in the diagram; the experimental curves are shown by dotted lines. These indicate in every case a progressive slowing up of the action as a result of the gradual disappearance of the catalyst. None of the curves, therefore, reaches the normal equilibrium value, although the curves for two samples, which had been recrystallised four times for these experiments, proceeded considerably further than the curves for two samples which had only been crystallised twice. The gradual disappearance of the catalyst at the boiling point of alcohol has already been noted (Lowry and Steele, T., 1915, **107**, 1385, footnote); the disappearance at atmospheric temperatures (20°) had not been noticed previously. The readiness with which alkali is eliminated by α′-chlorocamphor is remarkable, but the action appears to be only a simple reduction by alcoholic sodium ethoxide, giving aldehyde and camphor as the organic products of the action.

These curves show that in presence of equal quantities of a catalyst the bromo-compound changes more rapidly than the chloro-compound; and, since the isomeric change probably depends in each case on the slow formation of a trace of enol and its rapid return into the ketonic form, it may be concluded that enolisation takes place to a greater extent in the case of the bromo-compounds than in the case of the corresponding chloro-compounds.

Nitration.—Since the rotatory powers of the bromonitrocamphors for the green mercury line have not been recorded, parallel experiments were carried out on the nitration of α- and α′-bromocamphor, similar quantities of material being used in both cases. In the first instance, 3 grams of α-bromocamphor, boiled with 5 c.c. of nitric acid (d 1·4) during fifty hours, gave, after washing with water and a little alkali, a viscous oil which solidified on standing; after crystallising once from alcohol, the solid melted at 97° and gave $[\alpha]_{5461} - 20°$ in a 1 per cent. alcoholic solution; on recrystallisation, the melting point rose to 104° and the rotatory power to − 27°.

Under similar conditions, but after a nitration period of only seventeen hours, α'-bromocamphor gave an oil which solidified more readily; and after only one crystallisation the solid melted at 104° and gave $[\alpha]_{5461}$ − 25° in a 1 per cent. solution in alcohol. A duplicate experiment, in which nitration was carried on during twenty hours, gave a product which, after one crystallisation, melted at 104°, both alone and when mixed with a nitration product from α-bromocamphor, whilst its rotatory power was − 25·5°.

From these experiments it is clear that the nitration products from the two bromocamphors are identical, and that in the nitration of the new α'-compound the halogen is displaced by the nitro-group, which itself takes up the α'-position, whilst the bromine is transferred to the α-position.

Summary.

1. α'-Bromocamphor has been prepared from α-bromocamphor by the addition first of alkali, in order to render the isomerism dynamic, and then of acid, in order to make it static, the new compound prepared in this way being separated from the parent substance by fractional crystallisation.

2. α'-Bromocamphor melts at 78° (α- at 76°), has a density of 1·484 (α- is slightly lower), whilst $[\alpha]_{5461}$ = − 40° in alcohol as compared with + 169° for α-bromocamphor.

3. On the addition of alkali both isomerides pass to an equilibrium-mixture for which $[\alpha]_{5461}$ = + 149°. This corresponds with a mixture containing 92 per cent. of α-bromocamphor, whilst an estimate put forward in 1906 as a result of measurements of solubility with and without alkali gave 93 per cent. of the α-compound.

4. Whereas α- and α'-chlorocamphors yield stereoisomeric nitro-derivatives, the two bromocamphors, when nitrated, yield the same αα'-bromonitrocamphor. Analogous cases are referred to amongst aromatic compounds, where bromine and the nitro-group change places, whilst chlorine and the nitro-group remain fixed.

This work was begun at Guy's Hospital Medical School and completed at Cambridge. One of us (H. B.) is indebted to the Commissioners of the Exhibition of 1851 for a grant, with the help of which the work was carried to completion at Cambridge.

[*Received, March 2nd*, 1922.]

LXXIV.—*Introduction of the Chloroethyl Group into Phenols, Alcohols, and Amino-compounds.*

By George Roger Clemo and William Henry Perkin, jun.

It is well known that the ethyl ester of toluene-*p*-sulphonic acid may be employed for the ethylation of phenols; thus phenetole is readily obtained when phenol is treated with this ester in the presence of sodium carbonate. During the course of some investigations which are in progress, it became necessary to employ phenyl β-chloroethyl ethers, of which the simplest type is $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, and although substances of this type have, in a few instances, already been prepared from phenols by the action of ethylene dichloride in the presence of sodium hydroxide (Wohl and Berthold, *Ber.*, 1910, **43**, 2175), the process is troublesome and the yields are usually not more than 50 per cent. of those theoretically possible. It occurred to us that chloroethyl ethers of this kind might he made by acting on phenols in the presence of alkali with β-*chloroethyl toluene*-p-*sulphonate*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$. This substance has not been described, but we find that it is readily obtained in a yield of upwards of 90 per cent. by heating toluene-*p*-sulphonyl chloride with ethylene chlorohydrin and is a viscid syrup which distils at 210°/21 mm. without decomposition. This β-chloroethyl ester reacts readily with phenol in the presence of sodium hydroxide, yielding phenyl β-chloroethyl ether together with some diphenyl ethylene ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, the chloroethyl ether being obtained in a yield of 80 per cent. of that theoretically possible. o-*Tolyl* β-*chloroethyl ether* and p-*nitro*-o-*tolyl* β-*chloroethyl ether* were obtained from *o*-cresol and *p*-nitro-*o*-cresol in a similar manner. Experiment seems to indicate that when the nitro-group in phenols is *o*- or *p*- to the hydroxyl group, alkylation does not take place.

Phenyl β-chloroethyl ether reacts readily with aniline with the formation of β-*phenoxyethylaniline*, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$; the corresponding β-*phenoxydiethylaniline* from ethylaniline yields a characteristic p-*nitroso*-derivative, $NO{\cdot}C_6H_4{\cdot}NEt{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$. o-*Acetylaminophenyl* β-*chloroethyl ether*, $NHAc{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, is produced when *o*-acetylaminophenol is treated with the β-chloroethyl ester of toluene-*p*-sulphonic acid in the presence of sodium hydroxide.

Many other benzenoid derivatives of a similar kind have been prepared and investigated, and the ease with which they are formed suggests that β-chloroethyl toluene-*p*-sulphonate and esters of

analogous constitution may prove to be valuable reagents in synthetical work.

Derivatives of β-Naphthol.—In the case of the naphthols, the conversion into the β-chloroethyl ethers by the interaction with β-chloroethyl toluene-*p*-sulphonate proceeds with great ease. Thus β-naphthol yields β-*naphthyl* β-*chloroethyl ether*, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH_2Cl$, together with small quantities of di-β-naphthyl ethylene ether, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_{10}H_7$. When treated with ammonia, the chloroethyl ether is evidently converted into a mixture of the bases $C_{10}H_7 \cdot O \cdot C_2H_4 \cdot NH_2$, $(C_{10}H_7 \cdot O \cdot C_2H_4)_2NH$, and $(C_{10}H_7 \cdot O \cdot C_2H_4)_3N$, but the secondary base (m. p. 103—104°) is, so far, the only one of these which has been isolated in a pure condition and investigated. If dimethylamine is employed in the place of ammonia, the sole substance produced is β-*naphthyl* β-*dimethylaminoethyl ether*, $C_{10}H_7 \cdot O \cdot C_2H_4 \cdot NMe_2$, the hydrochloride of which has local anæsthetic action.

β-*Naphthyl* β-*chloroethyl ether (see above) is readily nitrated* in acetic acid solution, and the resulting 1-*nitro*-derivative is reduced by stannous chloride to 1-*amino*-β-*naphthyl* β-*chloroethyl ether*, $NH_2 \cdot C_{10}H_6 \cdot O \cdot CH_2 \cdot CH_2Cl$. This amino-derivative is converted into αβ-*naphthadihydroisooxazine*,

$$C_{10}H_6 <\begin{matrix} NH_2 \\ O \cdot CH_2 \cdot CH_2Cl \end{matrix} \longrightarrow C_{10}H_6 <\begin{matrix} NH \cdot CH_2 \\ O — CH_2 \end{matrix},$$

when it is boiled in amyl-alcoholic solution with potassium carbonate and a trace of copper powder.

*Action of β-Chloroethyl Toluene-*p*-sulphonate on Benzyl Alcohol.*—After it had been demonstrated that the β-chloroethyl ester interacts so readily with phenols, we were interested to ascertain whether the introduction of the chloroethyl group into aromatic alcohols could be accomplished under similar conditions, and selected benzyl alcohol for investigation. Experiment showed that this substance reacts readily with the β-chloroethyl ester in the presence of sodium hydroxide, yielding *benzyl* β-*chloroethyl ether*, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2Cl$. This substance interacts with diethylamine, producing β-*benzyloxytriethylamine*, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_2$, and this powerful base combines with ethyl iodide to yield β-*benzyloxytetraethylammonium iodide*, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_3I$.

*The Action of β-Chloroethyl Toluene-*p*-sulphonate on Aniline and Methylaniline.*—Aniline reacts readily with the β-chloroethyl ester in the presence of sodium carbonate, but we have been unable, so far, to isolate the initial product of the interaction, namely, β-chloroethylaniline, $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2Cl$, because under the conditions of experiment this substance immediately undergoes condensation with itself

and also with the other substances which are present at the moment of its formation. For this reason, the substances actually isolated were diphenylethylenediamine, $C_2H_4(NH{\cdot}C_6H_5)_2$, and diphenylpiperazine, $C_6H_5{\cdot}N(CH_2{\cdot}CH_2)_2N{\cdot}C_6H_5$.

In the case of methylaniline, the action of the β-chloroethyl ester in the presence of sodium carbonate leads mainly to the formation of dimethyldiphenylethylenediamine,

$$C_6H_5{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}C_6H_5,$$

but in this case it was also found possible to isolate some *β-chloroethylmethylaniline*, $C_6H_5{\cdot}NMe{\cdot}CH_2{\cdot}CH_2Cl$, an oil which condenses with β-naphthol in the presence of alkali yielding β-naphthyloxyethylmethylaniline, $C_{10}H_7{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}C_6H_5$ (compare von Braun, *Ber.*, 1917, **50**, 1637).

Experimental.

*β-Chloroethyl Toluene-*p*-sulphonate*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$.—This substance is readily prepared by boiling toluene-*p*-sulphonyl chloride (95 grams) with ethylene chlorohydrin (100 grams) in a reflux apparatus for three hours. Copious evolution of hydrogen chloride occurs at first, but this ceases after about two and a half hours. The excess of ethylene chlorohydrin (about 60 grams) is distilled off under about 250 mm., the residual syrup shaken with a little dilute sodium hydroxide and extracted with benzene. After drying over potassium carbonate and distilling off the benzene, the substance is fractionated under reduced pressure, when it distils at 210°/21 mm.; the yield is 102 grams or 87 per cent. of that theoretically possible (Found: C = 46·5; H = 4·7; Cl = 15·1; S = 13·6. $C_9H_{11}O_3ClS$ requires C = 46·1; H = 4·8; Cl = 15·3; S = 13·7 per cent.).

*β-Chloroethyl toluene-*p*-sulphonate* has a faint and not unpleasant odour and is a colourless syrup rather less viscous than glycerol; it is heavier than, and almost insoluble in, water.

Phenyl β-Chloroethyl Ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$.—This substance has already been prepared, in a yield of 48 per cent., by heating phenol with sodium hydroxide and ethylene dichloride under pressure (Wohl and Berthold, *loc. cit.*). A much better yield is obtained under the following conditions. Phenol (38 grams), sodium hydroxide (17 grams), water (30 c.c.), and β-chloroethyl toluene-*p*-sulphonate (94 grams) are heated in a water-bath for two to three hours with continuous stirring. The whole is then made strongly alkaline with sodium hydroxide and steam-distilled, when a pleasant-smelling oil (57 grams) passes over rapidly and afterwards a small quantity (1—2 grams) of diphenyl ethylene ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, crystallises in the condenser.

The oil was fractionated without preliminary drying, when, after a few grams had passed over, phenyl β-chloroethyl ether distilled constantly at 217—220°/760 mm., and, after solidification, melted at 28°. The yield—48 grams—can be increased by extracting the steam distillate with ether and distilling the dried extract.

o-*Tolyl β-chloroethyl ether*, $CH_3\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2Cl$, prepared in a similar manner from *o*-cresol, distils at 227—229°/762 mm., and p-*nitro*-o-*tolyl β-chloroethyl ether*, $CH_3\cdot C_6H_3(NO_2)\cdot O\cdot CH_2\cdot CH_2Cl$, obtained from *p*-nitro-*o*-cresol, separates from light petroleum in pale yellow prisms and melts at 66° (Found : N = 6·8. $C_9H_{10}O_3NCl$ requires N = 6·5 per cent.).

β-Phenoxyethylaniline, $C_6H_5\cdot NH\cdot CH_2\cdot CH_2\cdot O\cdot C_6H_5$, and p-*Nitroso-β-phenoxydiethylaniline*, $NO\cdot C_6H_4\cdot NEt\cdot CH_2\cdot CH_2\cdot O\cdot C_6H_5$.—Considerable quantities of β-phenoxyethylaniline have been prepared simply by boiling aniline (19 grams) with phenyl β-chloroethyl ether (15·6 grams) in a reflux apparatus for forty-eight hours. The reaction is accelerated by adding the equivalent quantity of sodium hydroxide, but with the disadvantage that the separation of sodium chloride is apt to cause bumping. The product is rendered strongly alkaline with sodium hydroxide, any excess of aniline and phenyl β-chloroethyl ether removed by distillation in steam, and the residue cooled, when the oil solidifies; the dry solid melts directly at 43—45° and weighs 16·8 grams. *β-Phenoxyethylaniline* separates from light petroleum in colourless plates and melts at 49—50° (Found : N = 6·6. $C_{14}H_{15}ON$ requires N = 6·6 per cent.).

The corresponding derivative of monoethylaniline was prepared in a similar manner and, after removing unchanged material by distillation in steam, the crude base was dissolved in dilute hydrochloric acid and converted into the *p*-nitroso-derivative by the addition of sodium nitrite. p-*Nitroso-β-phenoxydiethylaniline* separates from light petroleum in brilliant green prisms and melts at 94° (Found : N = 10·5. $C_{16}H_{18}O_2N_2$ requires N = 10·0 per cent.).

o-*Acetylaminophenyl β-Chloroethyl Ether*,

$$NHAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2Cl.$$

—In preparing this substance, *o*-acetylaminophenol (5 grams), sodium hydroxide (1·5 grams), water (3 c.c.), and β-chloroethyl toluene-*p*-sulphonate (7·8 grams) were mixed and heated in a water-bath with continuous stirring for six hours. On pouring the product into water, the oil solidified. The solid was collected, ground in a mortar with dilute alkali, washed, and dried, when 5·3 grams of nearly pure o-*acetylaminophenyl β-chloroethyl ether* remained. This substance separates from light petroleum in

colourless prisms and melts at 97—98° (Found: N = 6·4. $C_{10}H_{12}O_2NCl$ requires N = 6·5 per cent.).

p-*Acetylaminophenyl* β-*chloroethyl ether*, prepared in a similar manner from *p*-acetylaminophenol, crystallises from benzene in colourless prisms and melts at 126—127° (Found: N = 6·3 per cent.).

β-*Naphthyl* β-*Chloroethyl Ether*, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH_2Cl$.

This chloroethyl ether was produced when β-naphthol (30 grams), sodium hydroxide (8 grams), water (14 c.c.), and β-chloroethyl toluene-*p*-sulphonate (47 grams) were stirred and heated on the steam-bath for an hour. The oily product solidified on cooling, and was collected, ground with weak alkali, and dried on porous porcelain. In this condition it weighed 41 grams, melted at about 78°, and contained a small quantity of di-β-naphthyl ethylene ether, from which it was separated by extraction with light petroleum. On concentrating the solution, β-*naphthyl* β-*chloroethyl ether* separated in plates and melted at 83° (Found: Cl = 17·3. $C_{12}H_{11}OCl$ requires Cl = 17·2 per cent.).

α-*Naphthyl* β-*chloroethyl ether*, prepared in a similar manner from α-naphthol, melts at 28° and distils at 202°/16 mm. (Found: Cl = 16·8 per cent.).

Action of Ammonia and of Dimethylamine on β-*Naphthyl* β-*Chloroethyl Ether*.—When this chloroethyl ether is heated with concentrated aqueous ammonia in a sealed tube at 140°, a complex mixture of substances is obtained, from which, by crystallisation first from alcohol and then from light petroleum, ββ'-*di*-2-*naphthoxydiethylamine*, $(C_{10}H_7 \cdot O \cdot C_2H_4)_2NH$, was separated in prisms melting at 103—104° (Found: N = 3·8. $C_{24}H_{23}O_2N$ requires N = 3·9 per cent.).

In investigating the action of dimethylamine, the chloroethyl ether (3 grams) and alcoholic dimethylamine (12 c.c. of 14 per cent.) were heated in a sealed tube at 120—140° for sixteen hours. The alcohol was removed by evaporation, sodium hydroxide added, the base extracted with benzene and distilled under reduced pressure, when β-naphthyl-β-dimethylaminoethyl ether, $C_{10}H_7 \cdot O \cdot C_2H_4 \cdot NMe_2$, passed over at 200°/17 mm. and crystallised on cooling in ice, the melting point being approximately 16—17°. The *hydrochloride* was obtained in colourless crystals by passing dry hydrogen chloride into the benzene solution of the base. It melts at 185° and has local anæsthetic action (Found: N = 5·5. $C_{14}H_{17}ON,HCl$ requires N = 5·6 per cent.).

1-*Nitro*-β-*naphthyl* β-*Chloroethyl Ether*, $NO_2 \cdot C_{10}H_6 \cdot O \cdot CH_2 \cdot CH_2Cl$.—β-Naphthyl β-chloroethyl ether (20 grams) is dissolved in boiling

glacial acetic acid (200 c.c.), and nitric acid (60 c.c. of 63 per cent.) then gradually added so soon as the temperature has fallen to 45°, the whole being continuously stirred during the operation. After half an hour, the product is diluted with water, the yellow precipitate collected, washed well, and dried on porous porcelain. *The* 1-*nitro*-*derivative separates from acetic acid in pale yellow* prisms and melts at 120° (Found: N = 5·5. $C_{12}H_{10}O_3NCl$ requires N = 5·6 per cent.).

1-*Amino*-β-*naphthyl* β-*Chloroethyl Ether*, $NH_2\cdot C_{10}H_7\cdot O\cdot CH_2\cdot CH_2Cl$.—The above nitro-derivative (10 grams) was reduced by intimately mixing it with stannous chloride (26 grams) and heating with concentrated hydrochloric acid (80 c.c.) in a reflux apparatus for one and a half hours. The white tin double salt was collected, dissolved in hot water (2 litres), the tin removed by hydrogen sulphide, and the filtrate concentrated by distillation under reduced pressure in the presence of coal gas. The free *amino*-derivative (7·2 grams) was collected and recrystallised from light petroleum, from which it separated in leaflets melting at 85° (Found: N = 6·2. $C_{12}H_{12}ONCl$ requires N = 6·3 per cent.).

αβ-*Naphthadihydro*iso*oxazine*, $C_{10}H_6{<}\begin{matrix}NH\cdot CH_2\\ \vert \\ O—CH_2\end{matrix}$.—This interesting substance is obtained when the amino-derivative just described (2·2 grams) is mixed with potassium carbonate (1·4 grams), amyl alcohol (10 c.c.), and a trace of copper powder and heated to boiling in a reflux apparatus for two hours. The amyl alcohol is removed by distillation in steam, the residual oil extracted with light petroleum, dried over potassium carbonate, and distilled under reduced pressure. The distillate solidifies on cooling, and the mass, after draining on porous porcelain, is purified by recrystallisation from light petroleum, from which the iso*oxazine* separates in cubes melting at 44—45° (Found: C = 78·1; H = 5·8. $C_{12}H_{11}ON$ requires C = 77·8; H = 5·9 per cent.).

The Action of β-*Chloroethyl Toluene*-p-*sulphonate on* (*a*) *Aniline and* (*b*) *Methylaniline.*

(*a*) *Action on Aniline.*—Aniline (9·3 grams), the chloroethyl ester (23·5 grams), sodium carbonate (5·4 grams), and xylene (20 c.c.) were heated on the water-bath with continuous stirring for six hours. The product was acidified, the xylene removed by distillation in steam, and unchanged chloro-ester (6 grams) recovered by extraction with benzene. The acid liquid was made alkaline, steam-distilled, and the oily bases (4 grams) extracted from the distillate with ether (*A*); the residue in the distillation flask solidified and weighed 6 grams (*B*).

The oily bases (*A*) yielded with toluene-*p*-sulphonyl chloride and sodium hydroxide, 2 grams of the anilide soluble in alkali, corresponding with 0·7 gram of aniline. The portion insoluble in alkali crystallised from acetic acid in plates, melted at 223°, and consisted of *di(toluene-*p*-sulpho)diphenylethylenediamine*, $C_6H_5\cdot N(SO_2\cdot C_6H_4Me)\cdot CH_2\cdot CH_2\cdot N(C_6H_4Me\cdot SO_2)\cdot C_6H_5$.

The substance (*B*) was extracted with boiling methyl alcohol, when, on allowing to cool, diphenylpiperazine (m. p. 166°) separated first and subsequently, from the mother-liquors, the hydrochloride of diphenylethylenediamine (m. p. 230°) was obtained. The portion insoluble in boiling methyl alcohol was not further examined.

(*b*) *Action on Methylaniline.*—In this experiment, methylaniline (21·5 grams), the chloroethyl ester (23·5 grams), and sodium carbonate (10·6 grams) were heated at 105° with continuous stirring for seven hours. The product was steam-distilled and the mixture of bases (*C*, 5·5 grams) extracted from the distillate with ether; the residue in the distillation flask was made acid with hydrochloric acid and a small quantity of unchanged chloro-ester extracted with benzene. On adding sodium hydroxide to the aqueous solution, *s*-dimethyldiphenylethylenediamine, $C_6H_5\cdot NMe\cdot CH_2\cdot CH_2\cdot NMe\cdot C_6H_5$ (14 grams) was precipitated, and after crystallisation from methyl alcohol melted at 47°. The mixture of bases (*C*, 5·5 grams) was treated with toluene-*p*-sulphonyl chloride in the presence of alkali * and yielded a semi-solid mass which, on washing with dilute hydrochloric acid, left 4·3 grams of toluene-*p*-sulphonmethylanilide, $C_6H_5\cdot NMe\cdot SO_2\cdot C_6H_4Me$ (m. p. 94°), corresponding with 1·7 grams of methylaniline. The hydrochloric acid washings were made alkaline with sodium hydroxide and extracted with ether, when *β-chloroethylmethylaniline* (3·8 grams), $C_6H_5\cdot NMe\cdot CH_2\cdot CH_2Cl$, was

* Toluene-*p*-sulphonyl chloride is a very useful reagent for characterising primary and secondary amino-compounds and for the estimation of primary, secondary, and tertiary amino-derivatives in mixtures. In the case, for example, of a mixture of aniline, methylaniline, and dimethylaniline, the bases are left with excess of the sulphonyl chloride and aqueous potassium hydroxide (12 per cent.) for several hours. The whole is acidified, filtered, and the tertiary base (dimethylaniline) recovered from the acid solution by the addition of alkali and extraction with ether. The residue is warmed on the water-bath with excess of aqueous potassium hydroxide until all unchanged sulphonyl chloride has been decomposed, during which time the derivative of the primary base (aniline) dissolves, leaving the derivative of the secondary base (methylaniline), which may be weighed and identified by recrystallisation from methyl alcohol, etc. Finally, the derivative of the primary base is precipitated from the alkaline solution by hydrochloric acid, weighed, and recrystallised from methyl alcohol. This process is only applicable to bases which react readily with toluene-*p*-sulphonyl chloride under the conditions mentioned.

obtained, boiling at 124°/10 mm. This base, which does not appear to have previously been described, was digested with β-naphthol and a solution of potassium hydroxide in acetone, when it yielded *β-naphthoxyethylmethylaniline*, $C_{10}H_7 \cdot O \cdot CH_2 \cdot CH_2 \cdot NMePh$, which crystallised from methyl alcohol in colourless plates and melted at 73—75° (Found: C = 82·2; H = 6·9; N = 4·9. $C_{19}H_{19}ON$ requires C = 82·3; H = 6·9; N = 5·0 per cent.).

*Action of β-Chloroethyl Toluene-*p*-sulphonate on Benzyl Alcohol. Formation of Benzyl β-Chloroethyl Ether*, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2Cl$.

In the preparation of this substance, benzyl alcohol (32·5 grams), the chloroethyl ester (72 grams), sodium hydroxide (13 grams), and water (80 c.c.) were continuously stirred and heated on the water-bath for four hours. On distillation in steam, *benzyl chloroethyl ether* passed over as an oil possessing a pronounced odour of oranges. This was extracted with benzene, weighed 15 grams, and distilled at 95—110°/16 mm.

Action of Diethylamine.—In studying this interesting action, benzyl chloroethyl ether (9·5 grams), dissolved in alcohol (15 c.c.), was mixed with diethylamine (8 grams) and heated in a sealed tube at 180—190° for eight hours. The product was acidified and distilled in steam, but very little oil passed over; sodium hydroxide was then added and the distillation continued, when, after extraction with benzene, a base (7 grams) was obtained which distilled at 146°/12 mm. (Found: C = 76·1; H = 10·3; N = 6·7. $C_{13}H_{21}ON$ requires C = 75·4; H = 10·1; N = 6·7 per cent.).

β-Benzyloxytriethylamine, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_2$, is sparingly soluble in water and yields readily soluble salts with hydrochloric and sulphuric acids. When the base is warmed with ethyl iodide, combination takes place readily and *β-benzyloxytetraethylammonium iodide*, $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_3I$, separates as a white solid, which crystallises from acetone in colourless plates melting at 105°.

We are indebted to the British Dyestuffs Corporation for permission to publish these results.

DYSON PERRINS LABORATORY,
OXFORD.
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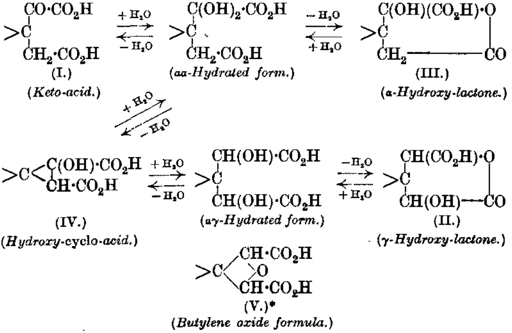
LXXV.—*Ring-chain Tautomerism. Part I. The Occurrence and Effect of Keto-enol Tautomerism between a Ring Compound and its Open-chain Isomeride.*

By George Armand Robert Kon, Arnold Stevenson, and Jocelyn Field Thorpe.

The work which has been carried out in these laboratories during the past seven years has shown conclusively that the angle between any two valencies of a carbon atom is altered profoundly by the attachment of groups to the remaining two valencies or by their inclusion in a cyclic complex. Moreover, it has been proved that the alteration of the angle affects to a marked degree the reactions of the substances in which such alteration occurs and that the general effect reveals itself in quite a number of characteristic ways. One of these, and one which appears to afford an easy means of detecting the effect, is supplied by the formation and properties of those derivatives of acids belonging to the glutaric series which may be regarded, in an empirical sense, as having been derived from the acid by the replacement of two of its hydrogen atoms by an oxygen atom. There are five structural isomerides of this type, if it is assumed that the two remaining valencies of the β-carbon atom are attached either to groups or are included in a cyclic complex, and these may be formulated as in I, II, III, and IV.

It is evident that all these forms are mutually interconvertible through two hydrated forms thus:



* This formula is discussed on page 655.

the two hydrated forms being interconvertible only through the ring form (IV).

The changes represented above involve the alternate addition and elimination of water, but it is evident that they can also be regarded as tautomeric changes * of the keto-enol type, provided that the atoms forming any of the potentially tautomeric systems are sufficiently close together to enable the mobile hydrogen atom to pass between the oxygen and the carbon atom concerned. For example, keto-enol tautomerism (chain type) is represented thus:

$$\text{Type A.}\qquad \mathrm{CH{\cdot}C{:}O \rightleftharpoons C{:}C{\cdot}OH}$$

and it can be assumed that if the conditions which allow keto-enol tautomerism are present in an open-chain and a ring compound, that is to say, if the distance apart of the atoms forming the tautomeric complex of the keto-enol type A is comparable with that of the atoms forming a potentially tautomeric system between an open-chain and a ring compound, the possibility of the occurrence of a new type of tautomerism, which may be termed the ring-chain type, arises. Two examples may be given in the ring-chain types B and C—

$$\text{Type B.}\qquad \overbrace{\mathrm{C(OH){\cdot}O{\cdot}OC}}^{C_n} \rightleftharpoons \overbrace{\mathrm{C{:}O\quad HO{\cdot}OC}}^{C_n}$$

$$\text{Type C.}\qquad \overbrace{\mathrm{C(OH){\cdot}CH}}^{C_n} \rightleftharpoons \overbrace{\mathrm{C{:}O\quad CH_2}}^{C_n},$$

and it will be noticed that the interconvertibility of the substances mentioned on page 650 may fall within the tautomerism of either one type or the other—

$$>\mathrm{C}<\begin{matrix}\mathrm{C(OH){\cdot}CO_2H}\\ \mathrm{CH{\cdot}CO_2H}\end{matrix} \rightleftharpoons >\mathrm{C}<\begin{matrix}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix} \rightleftharpoons >\mathrm{C}<\begin{matrix}\mathrm{C(OH)(CO_2H){\cdot}O}\\ \mathrm{CH_2\text{———————}CO}\end{matrix}$$

Type C. Type B.

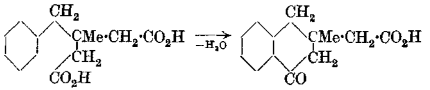
There can be no question that, under favourable conditions, tautomerism of both types B and C can occur. For example, tautomerism of type B is, in all probability, the cause of the mutarotation of the sugars and the interconvertibility of the α- and β-forms in solution.

* The word tautomerism is used to denote reversible isomeric change, such change being brought about in solution, or in the liquid state with or without the aid of catalysts, to form equilibrium mixtures of the individuals showing tautomerism. Solid substances of definite melting point are assumed to be single individuals. When the change is not reversible, the substances are called isomeric. When the change from one individual to another is effected by one reagent or process and the reverse change by another, the substances are regarded as isomeric and not tautomeric.

Another good example is that supplied by the opianic acids (*m*-opianic acid) (Fargher and Perkin, T., 1921, **119**, 1728), and by 4 : 5-dimethoxyphthalonic acid,* substances which exhibit tautomerism leading to precisely the same kind of reactions as those shown by *isatin, the tautomeric character* of which *is not open to question.* The sole difference between the two types is that the one is accompanied by the fission of the ring and the other is not.

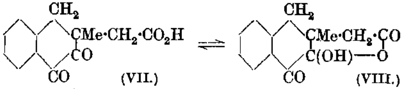
Tautomerism of type C has been recorded in the well-known anthrol-anthrone change and also in the transformation of *apo*tricyclol into camphenilone (Lipp and Padberg, *Ber.*, 1921, **54**, [*B*], 1327), although in this case the reverse change, corresponding *with the reaction mentioned on p. 650, has not yet been effected.*

We were led, in the first instance, to investigate tautomerism of this kind on account of the discovery of a remarkable substance which was produced during experiments having for their object the determination of the structure of substance VI, which Kon and Stevenson (T., 1921, **119**, 87) prepared in accordance with the scheme—



(VI.)

The proof of structure of this compound was determined by its ultimate oxidation to phthalic acid, but it had been noticed that, *under certain conditions* described *in* the experimental portion, *it* was transformed into an intermediate product, melting at 171°, which, in its reactions, behaved as if it had either of the two formulæ VII and VIII—



(VII.) (VIII.)

(*Coloured form.*) (*Colourless form.*)

Thus, among reactions to be described, it combined with *o*-phenylenediamine to form a quinoxaline in accordance with VII, and gave with acetyl chloride an acetyl derivative in accordance with VIII.

* We are informed by Professor W. H. Perkin (private communication) that the change keto-acid ⟶ hydroxy-lactone is effected by drying the first-named, which crystallises with $2H_2O$, in ethereal solution with sodium sulphate. The change hydroxy-lactone ⟶ keto-acid is brought about by alkali. There is thus no evidence at present to show that the interchange is reversible in the sense required by the definition of tautomerism given on p. 651.

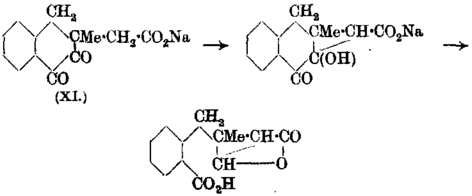
When oxidised with hydrogen peroxide it passed into the tribasic acid,

$$\text{(IX.)}\quad (o)CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CMe(CO_2H){\cdot}CH_2{\cdot}CO_2H.$$

The most remarkable property of the substance, however, is shown in its behaviour towards solvents. Its solution in water or alcohol is colourless at the ordinary temperature, but acquires a marked yellow colour when warmed. The colour disappears when the solution is again brought to the ordinary temperature. In dry, *non-hydroxylic solvents such as benzene the same change occurs,* although the discharge of colour is noticeahly slower. It seems to us that the only explanation of these pheuomena must be hased on the assumption that the lactone form (VIII) is colourless whilst the diketo-form (VII) is yellow. The solid, colourless form melting at 171° is the single lactone individual (VIII), but in solution it at once tends to form an equilibrium mixture with the diketo-form (VII). *In water at the ordinary temperature, the amount of the* diketo-form in the equilihrium mixture is too small to be detected by the eye, but as the temperature rises more of the coloured form is produced, to disappear again when the temperature falls. The change must therefore be one of ring-chain tautomerism of type B.

Owing to the alteration of colour which accompanies the tautomeric change and by which it can he measured, the compound *should prove a valuable source of information respecting the* influence of temperature, solvents, etc., on this type of tautomerism.

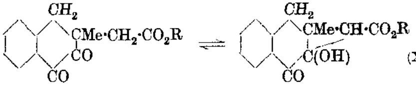
There is still another remarkable reaction which the substance melting at 171° undergoes. On boiling with dilute caustic alkali, the marked yellow colour of the solution soon disappears, and the product is found to be the alkali salt of a new acid melting at 187°. This acid is the lactone of a dibasic acid and is isomeric with the *acid melting at 171°. The reactions of the new acid show that it* possesses the structure X, and its formation can be represented in the following way—



(XI.)

(X.)

Owing to the fission of the six-membered ring during the final stage of the reaction, it is impossible to say if the interchange is reversible.

(XII.)  (XIII.)

However, when taken in conjunction with certain other experiments which are now being carried out by Mr. Deshapande of this laboratory, which will shortly be published, and which show that the change—

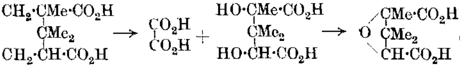
$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}CO\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix} \rightleftharpoons \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}C(OH)\cdot CO_2H\\CH\cdot CO_2H\end{matrix}$$

can be effected in the presence of alkali and is reversible, there can be little doubt that, could the intermediate product (XIII) be isolated, it would show tautomerism of type C with its isomeride (XII).

It follows *therefore that this truly remarkable substance melting* at 171° can exhibit ring-chain tautomerism of both type B and type C, the former when the lactone ring is capable of existence and the latter when its formation is prohibited by the presence of alkali. It is evident that a sodium salt of formula (XI) can no longer exhibit tautomerism of type B.

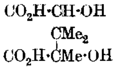
When the literature was searched for other possible examples of the tautomeric types B and C, we were struck by the rather curious properties possessed by an acid of the empirical formula $C_8H_{12}O_5$ which Balbiano (*Rend. Accad. Lincei*, 1892, I, 278; *Ber.*, 1895, **27**, 2133) had prepared by the oxidation of camphoric acid. Balbiano showed that the acid $C_8H_{12}O_5$ passed into a dibasic acid of the formula $C_8H_{14}O_4$ on reduction, and this acid was shown to be αββ-trimethylglutaric acid, $CO_2H\cdot CH_2\cdot CMe_2\cdot CHMe\cdot CO_2H$, by Perkin and Thorpe, who prepared it synthetically (T., 1899, **75**, 61), a discovery which Balhiano had predicted (*Ber.*, 1896, **28**, 1506). He considered, at that time, that his acid $C_8H_{12}O_5$ contained a hydroxyl group, because he was able to prepare both an acetyl and a benzoyl derivative from the dimethyl ester. He did not at this stage assign any definite formula to his acid. Mahla and Tiemann (*Ber.*, 1896, **28**, 2151) repeated Balhiano's work in the hope of obtaining evidence in support of the latter's formula for camphoric acid. They were able to isolate the acid $C_8H_{12}O_5$, but considered it to be α′-keto-αββ-trimethylglutaric acid, $CO_2H\cdot CO\cdot CMe_2\cdot CHMe\cdot CO_2H$, because on being heated it was converted into carbon monoxide and

trimethylsuccinic anhydride. They were unable, however, definitely to establish the ketone character of the acid, for although they prepared derivatives by the action of hydroxylamine and of *p*-bromophenylhydrazine, the compounds formed were ill-defined and were not analysed. Balbiano, in a final paper on this subject (*Ber.*, 1897, **30**, 289), showed that the *p*-bromophenylhydrazone of Mahla and Tiemann was, in fact, an addition product and not a hydrazone. In this paper he puts forward the oxide formula (XIV) as being the one most in accordance with the facts, and considers that its formation from camphoric acid can be represented by the scheme

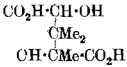
 (XIV.)

It is a curious fact that Balbiano seems to have forgotten his earlier experiments, which proved the presence of a hydroxyl group in the dimethyl ester of his acid, but he states that the diethyl ester reacts neither with hydroxylamine nor with *p*-bromophenylhydrazine.

The scheme of formation of the acid from camphoric acid suggested by Balbiano is reasonable, and the oxide formula accounts for its behaviour on reduction. The formula is nevertheless an unusual one, and has as yet found no analogue among the acids of the glutaric series, although a great deal of work has been done on these compounds during the past twenty years. Moreover, the formula is highly improbable for the following reasons. The formation of the oxide must take place through one or other of the theoretically possible forms of the dihydroxy-acid (XV) and (XVI) by the elimination of water :

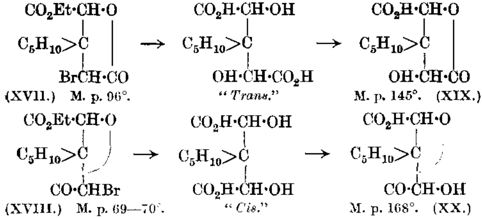
(XV.) 

"*Cis.*"

 (XVI.)

"*Trans.*"

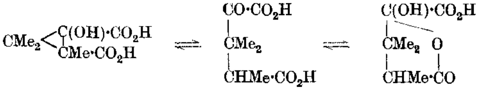
Now there is ample evidence to show how *cis*- and *trans*-forms of dihydroxy-acids of this type behave on dehydration, because the *cis*- and *trans*-bromolactone esters (XVII) and (XVIII) in the *cyclo*hexane series have been proved (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1089) to pass on treatment with alkali through the corresponding dihydroxy-acids, to the *cis*- and *trans*-forms of the corresponding lactones (XIX) and (XX).



(XVII.) M. p. 96°. "*Trans.*" M. p. 145°. (XIX.)
(XVIII.) M. p. 69—70°. "*Cis.*" M. p. 168°. (XX.)

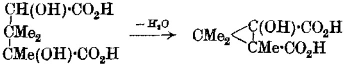
There was no evidence whatever to show that any tendency existed to form the butylene oxide ring by the elimination of water between the hydroxyl groups.* The production of a compound having Balbiano's oxide formula by the elimination of water from a precisely similar dihydroxy-acid in the trimethyl series is, therefore, in the highest degree unlikely.

The keto-formula (XXI) of Mahla and Tiemann must next be considered, and, in the light of what has been already written, it might be expected that the compound would be tautomeric with its hydroxy-lactone isomeride (XXII) (Type B), and also, possibly,



(XXIII.) (XXI.) (XXII.)

with the ring hydroxy-acid (XXIII) (Type C). The chief objection to this explanation is that neither of the tautomeric individuals (XXI) or (XXII) can be represented as having been produced from camphoric acid by the elimination of water from the αα′-dihydroxy-acid. On the other hand, it is obvious that the ring hydroxy-acid (XXIII) can be represented as having been produced in this way :

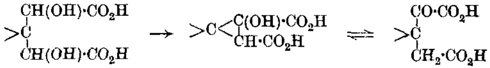


If it can be assumed that in Balbiano's acid there are structural conditions present which render it possible for tautomerism to occur between the three substances XXI, XXII, and XXIII, explanations

* It must be noted, however, that both bromolactones yield considerable quantities of the hydroxy-ring acid, $C_5H_{10}{>}C{<}^{C(OH)\cdot CO_2H}_{CH\cdot CO_2H}$, on treatment with strong alkali (*loc. cit.*, p. 1103).

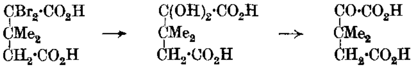
are provided, not only for all the reactions of Balbiano's acid hitherto described, *but also for those which are recorded in this paper.*

In the first place, it is desirable to ascertain if it is justifiable to assume that the change



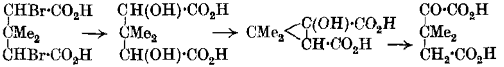
is likely, and in this connexion valuable evidence can be obtained by considering the reactions and the methods of formation of the ketoglutaric acids.

The first acid of this series to be prepared was α-keto-ββ-dimethylglutaric acid (XXIV), *which was produced by the action of alkali* on ethyl hydrogen dibromo-ββ-dimethylglutarate (Perkin and Thorpe, T., 1901, **79**, 729). At the time it was assumed that this dibromo-salt was the αα-derivative (XXV) entirely because it yielded the keto-acid in the manner described :



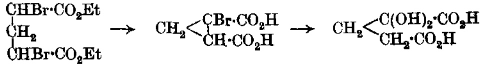
(XXV.) (XXIV.)

There is, as it happens, no need to make this assumption, for in all probability it was the αα'-dibromo-derivative which reacted either in accordance with the scheme :



or with the intermediate formation of a 1-bromo*cyclo*propanedicarboxylic acid in place of the dihydroxy-acid.

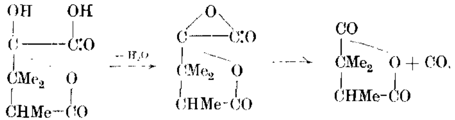
This follows, not only because the formation of other asymmetrically brominated derivatives of the glutaric acids has not since been observed despite the numerous acids of this group which have been brominated, but also because in the very comprehensive experiments of Ingold (T., 1921, **119**, 306) it is clearly shown that the reaction



occurs in the presence of alkali. The possibility of the formation of the keto-acid from camphoric acid is thus established.

Again, one of the most characteristic reactions of Balbiano's

acid is the ease with which it is converted into carbon monoxide and trimethylsuccinic anhydride when it is heated above its melting point. This decomposition, which is shown by all the so-called ketoglutaric acids which we have examined, is not quantitative, the percentage of carbon monoxide evolved varying in every case, but always being less than one gram-molecule. With concentrated sulphuric acid similar varying results are obtained, although with this reagent the amount of carbon monoxide is always in excess of one gram-molecule but is never equal to two, the figures obtained being embodied in a table given on page 665. The course of the reactions by which a hydroxy-lactone of formula XXII is converted into carbon monoxide and the anhydride of the acid next lower in the series in the absence of reagents can be readily understood if it is assumed that dehydration occurs first and that then carbon monoxide is eliminated, thus :

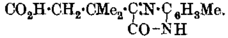


A decomposition of this kind cannot be explained on either a keto-formula or on a hydroxy-ring structure, and it can therefore be assumed that the amount of an acid, which, when heated alone, is converted into carbon monoxide and the anhydride of the acid next lower in the series, is a direct measure of the amount of hydroxy-lactone present under the experimental conditions employed.

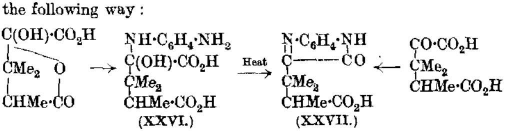
The reason why the amounts of carbon monoxide evolved when the acids are treated with concentrated sulphuric acid are always less than two gram-molecules and greater than one is at present an open question, although it must be pointed out that an adequate explanation is provided if it is assumed that the concentrated sulphuric acid first converts the hydroxy-form present under the experimental conditions used into carbon monoxide and the anhydride of the next lower homologue—an assumption which is warranted by the fact that the anhydride can always be obtained from the product of the reaction—and that the residue other than the anhydride is then acted on by the concentrated acid to give two gram-molecules of carbon monoxide. The nature of the second reaction, and indeed the behaviour of ketoglutaric acids generally, is being investigated.

It would be very difficult to devise any scheme which would show the course of the reactions by which a substance of Balbiano's

butylene oxide formula could be converted into carbon monoxide and trimethylsuccinic anhydride on being heated (see also Fargher and Perkin, *loc. cit.*, p. 1737, for a description of the conversion of 4 : 5-dimethoxyphthalonic acid into *m*-hemipinic acid by means of sulphuric acid).

The best reagent for the characterisation of α-keto-ββ-dimethylglutaric acid was found by Perkin and Thorpe (*loc. cit.*) to be *o*-tolylenediamine, which reacted in acetic acid solution to form a *condensation product of the formula* 

We *have carried out a similar reaction with o-phenylenediamine*, and find that in the case of the dimethyl-acid the condensation product is rapidly and quantitatively precipitated when the reacting substances are warmed. The same is the case with other keto-glutaric acids which are mentioned in the experimental portion, and notably with ketoglutaric acid itself. When, however, the reaction is applied to Balbiano's acid, evidence is obtained which indicates the tautomeric character of the substance. When, for example, the *acid is treated with o*-phenylenediamine in acetic acid solution, the condensation product (XXVII) is precipitated on boiling for a short time to the extent of approximately 50 per cent., the *remainder being a more soluble substance, an addition product* (XXVI), which passes when heated a few degrees above its melting point into the condensation product (XXVII) and water. It can be shown to be an addition product of type (XXVI) by the fact that its aqueous solution is acid and that this solution does not yield *o*-phenylenediamine when rendered alkaline. In other words, it is not a mere salt of acid and base. The formation of this addition product, which recalls the compounds obtained by Mahla and Tiemann by means of hydroxylamine and *p*-bromophenylhydrazine, taken in conjunction with the formation of the true condensation product of the keto-acid, furnishes strong evidence of the tautomeric character of Balbiano's acid, the reactions being represented in the following way:



(XXVI.) Addition product. (XXVII.) Condensation product.

The explanation we wish to put forward is that the changes:

Keto-acid ⇌ Hydroxy-ring acid ⇌ Hydroxy-lactone acid

are in the case of Balbiano's acid tautomeric, that is, reversible in solution or in the presence of catalysts, and that whereas the solid acid melting at 120° is the hydroxy-lactone form, it reacts in solution or towards reagents either in the keto-form or in the hydroxy-ring form. Strong evidence in favour of the occurrence of the hydroxy-ring phase * is provided, not only in the production of the keto-acid from camphoric acid already discussed, but also from the occurrence of an acetyl and a benzoyl derivative of the dimethyl ester described by Balbiano. The dimethyl ester prepared by him is a substance of definite boiling point, and the analytical figures show that it is the dimethyl ester of the open-chain ketonic acid (XXI), and not the methyl ester of the hydroxy-lactone acid (XXII) as suggested by Mahla and Tiemann (*loc. cit.*); moreover, Balhiano's figures for the acetyl and benzoyl derivatives do not agree with those required by the respective derivatives of the latter methyl ester, but agree much more closely with those which would be given by the corresponding derivatives of the dimethyl ester of the cyclic acid (XXIII). It will be evident that the formation of the dimethyl ester prevents tautomerism of type B, because the necessary mobile hydrogen is lacking. If we can assume that tautomerism of type C now comes into play,

$$\begin{array}{l} CO\cdot CO_2Me \\ | \\ CMe_2 \\ | \\ CHMe\cdot CO_2Me \end{array} \rightleftharpoons CMe_2{<}\begin{array}{l} C(OH)\cdot CO_2Me \\ | \\ CMe\cdot CO_2Me \end{array},$$

the formation of an acetyl and a benzoyl derivative can be explained.

It is evident that much more work remains to be done before these important questions can be settled. Reversibility or non-reversibility, tautomerism or isomerism must certainly be functions of the distance apart of the iuteracting elements, or, in other words, of the tetrahedral angle of the complex involved. It would appear that in the trimethyl-substituted glutaric acid and in the diketone of formula (VII) there is present just the necessary condition to enable tautomerism of both type B and type C to occur. In how far this is true of other substances experiments which are now in progress will determine.

EXPERIMENTAL.

Lactone of ac-1-*Keto-2-hydroxy-3-methyltetrahydronaphthalene*-3-*acetic Acid* (VIII).

Ten grams of *ac*-1-keto-3-methyltetrahydronaphthalene-3-acetic acid (VI) were dissolved in sodium hydroxide solution and a 1 per

* There is, at present, no evidence to show that the changes in the case of the hydroxy-ring acid are reversible. It must be remembered, however, that the change keto-acid–hydroxy-ring acid has been shown to be reversible in the case of the diethyl acid (see p. 654).

cent. solution of potassium permanganate added until the colour persisted, the operatiou being carried out at about 10°. After destroying the excess of permanganate with sulphurous acid and filtering, hydrochloric acid was added to the filtrate, when a copious precipitate was formed, yielding 10 grams of the crude product. On dissolving in hot dilute alcohol, the solution became yellow, but the colour disappeared as the solution cooled, and the substance separated out in large plates, which shrank at 168° and melted at 171°. This yellow colour is noticeable, not only in water, but also in non-hydroxylic solvents such as benzene or acetone. A dilute aqueous solution, for example, is colourless, but becomes markedly yellow when boiled. On cooling, the colour is discharged (Found: C = 67·43; H = 5·32. $C_{13}H_{12}O_4$ requires C = 67·23; H = 5·21 per cent.). The lactone does not effervesce with aqueous sodium hydrogen carbonate; it dissolves in concentrated sulphuric acid to give a bright orange solution, but on dilution the colour disappears and the original compound is reprecipitated. The *silver* salt, which must be that of the tautomeric diketonic acid, is somewhat soluble in water and should be washed with dilute alcohol (Found: Ag = 31·59. $C_{13}H_{11}O_4Ag$ requires Ag = 31·83 per cent.). The mercuric, lead, cupric, chromium, ferric, and ferrous salts form readily in the cold from the ammonium salt, whilst the barium and calcium salts are soluble both in the cold and on warming.

The lactone was also obtained by heating the parent substance (VI) on the steam-bath with 50 per cent. nitric acid until fumes ceased to be evolved. On evaporation, a solid residue was obtained, which after purification proved to be identical with the compound prepared by the method described above.

The *acetyl* derivative of the formula in accordance with VIII was prepared by heating under reflux 3 grams of the substance with 10 c.c. of acetyl chloride until complete solution took place. On evaporation, there remained an oil, which solidified in a vacuum, yielding 3 grams of crude product. Recrystallised twice from chloroform, it formed thick, square plates, which melted at 142° (Found: C = 65·64; H = 5·33. $C_{15}H_{14}O_5$ requires C = 65·47; H = 5·14 per cent.).

The *quinoxaline* derived from VII was obtained by heating together alcoholic solutions of the lactone (1·1 grams) and of *o*-phenylenediamine (0·5 gram), a precipitate forming as the liquid cooled. The reaction also takes place slowly in the cold, and in both cases good yields are obtained. On recrystallisation from alcohol, the quinoxaline separated in plates which sintered slightly at 170° and melted sharply at 177° (Found: C = 74·69; H = 5·30; N = 9·42. $C_{19}H_{16}O_2N_2$ requires C = 74·95; H = 5·29; N = 9·21

per cent.). It is a monobasic acid, thus showing that the carboxyl group of the original compound is not affected by the reaction [Titration with $N/10$-sodium hydroxide. Found: 13·20 c.c. Calc. (monobasic), 13·05 c.c.].

The *semicarbazone* was prepared by warming an alcoholic solution with semicarbazide acetate. On keeping, a dense yellow precipitate formed, which on recrystallisation from alcohol separated in pale yellow plates which melted sharply at 212° and then decomposed (Found : N = 14·89. $C_{14}H_{15}O_4N_3$ requires N = 14·53 per cent.).

The *oxime* was readily formed. Recrystallised from dilute alcohol, it separated in minute prisms melting at 183° (Found : N = 5·73. $C_{13}H_{13}O_4N$ requires N = 5·67 per cent.).

A p-*nitrophenylhydrazone* was obtained by heating under reflux for eight hours alcoholic solutions of the lactone and of *p*-nitrophenylhydrazine. On diluting and rubbing, a brick-red precipitate formed, which on recrystallisation from alcohol separated in small, thick, orange plates melting at 180° (Found : N = 11·65. $C_{19}H_{17}O_5N_3$ requires N = 11·44 per cent.).

α-o-*Carboxybenzyl-α-methylsuccinic Acid* (IX).

The oxidation to the above tribasic acid was effected by dissolving 1 gram of the lactone in sodium carbonate solution and adding 35 c.c. of a 6 per cent. solution of hydrogen peroxide, when the yellow colour rapidly disappeared. After sixteen hours the solution was acidified with hydrochloric acid and extracted with ether, the ethereal extract yielding more than 1 gram of crude acid. On dissolving in water and then adding hydrochloric acid, it was precipitated in microscopic prisms melting at 187° with violent decomposition [Found : C = 58·68; H = 5·65. $C_{13}H_{14}O_6$ requires C = 58·62; H = 5·30 per cent. Titration with $N/20$-sodium hydroxide. Found: 21·8 c.c. Calc. (tribasic), 21·6 c.c.].

*Lactone of 3-Hydroxy-2-*o*-carboxybenzyl-2-methyl*cyclo*propane-1-carboxylic Acid* (X).

The substance melting at 171° was dissolved in excess of 10 per cent. sodium hydroxide solution and heated under reflux for two to three hours. When cold, it was acidified with hydrochloric acid and extracted with ether, the ethereal extract giving a 60—70 per cent. yield of the crude isomeride. The reaction takes place slowly at 20°. Recrystallised from water with the addition of a few drops of alcohol, it separated in small plates melting at 187—188° (Found : C = 67·02; H = 5·38. $C_{13}H_{12}O_4$ requires C = 67·21; H = 5·21 per cent.). On adding silver nitrate to a neutral solution of the ammonium salt, the *silver* salt of the corresponding dibasic hydroxy-

acid is precipitated, the operation being best carried out in the presence of alcohol (Found: Ag = 46·37. $C_{13}H_{12}O_5Ag_2$ requires Ag = 46·51 per cent.). Unlike its isomeride, it effervesces with *aqueous sodium hydrogen carbonate, and the barium and calcium* salts are precipitated on heating, the salts of the heavy metals being, as before, readily formed. It does not react with semicarbazide or acetyl chloride.

If further oxidised with 3 per cent. alkaline potassium permanganate at 100°, both this lactone and its isomeride (VIII) pass into a substance which on recrystallisation from water melts at 210° and has the empirical formula $C_{13}H_{10}O_5$ (Found: C = 63·43; H = 4·34. Calc., C = 63·40; H = 4·10 per cent.). The change also takes place slowly at 20°, some days being required for complete oxidation. The substance effervesces with sodium hydrogen carbonate solution, and titration with *N*/10-sodium hydroxide shows that it is dibasic (Found: 11·05 c.c. Calc., 11·25 c.c.). A silver salt could not, however, be obtained, as this is very soluble even in alcoholic solution, so that it is impossible to say if it is a true acid or a lactone. It does not react with semicarbazide, but it contains one hydroxyl group, shown by the formation of an acetyl derivative melting at 218—219° (Found: C = 62·24; H = 4·22. $C_{15}H_{12}O_6$ requires C = 62·48; H = 4·20 per cent.). Further *investigation is, however, necessary before a definite structure can* be assigned to it.

α-Keto-ββγ-trimethylsuccinic Acid (*Balbiano's Acid*) (XXI).

The acid was prepared in accordance with the directions given by Balbiano (*loc. cit.*). The precipitate obtained on boiling with excess of calcium chloride solution was dissolved in hydrochloric acid and extracted with ether; the ethereal extract was neutralised with sodium hydroxide and again treated with a 15 per cent. calcium chloride solution. The precipitate, which again formed on boiling, was recrystallised from water (Mahla and Tiemann, *loc. cit.*), the salt separating, on cautious evaporation, in clusters of spherical nodules. These were dissolved in moderately dilute hydrochloric acid and extracted with ether, the ethereal extract yielding the acid, which, after rubbing with chloroform, melted at 120° [Titration with *N*/20-sodium hydroxide. Found: 14·5 c.c. Calc. (dibasic), 14·6 c.c.].

The addition product with *o*-phenylenediamine (XXVI) was prepared by mixing 1 gram of the acid dissolved in water and 1 gram of *o*-phenylenediamine hydrochloride in sodium acetate solution. On standing and rubbing, a dense precipitate formed which could not be satisfactorily recrystallised owing to its great

solubility in the usual solvents. The crude substance, which melted at 148°, was therefore analysed (Found: C = 56·54; H = 6·82; N = 9·88. $C_{14}H_{20}O_5N_2$ requires C = 56·73; H = 6·79; N = 9·45 per cent.). It was not the neutral salt, because its solution was distinctly acid to litmus and it was not decomposed by sodium hydroxide solution. When it was heated a few degrees above its melting point, water was given off and a grey deposit formed on the sides of the containing vessel. This, after purification, proved to be identical with the condensation product described below.

The condensation product with *o*-phenylenediamine (XXVII) was made by boiling an aqueous solution of the compound described above, when approximately 50 per cent. of the theoretical quantity separated as a grey precipitate. Recrystallised from alcohol, it separated in grey scales which softened at 220° and melted at 223—224° (Found: C = 64·60; H = 6·27; N = 11·14. $C_{14}H_{16}O_3N_2$ requires C = 64·59; H = 6·19; N = 10·77 per cent.).

The method adopted for estimating the amounts of carbon monoxide evolved was to heat the acid in a small resistance-glass tube provided with inlet and outlet tubes so that the gas could be swept out with carbon dioxide. The carbon monoxide given off was collected in a nitrometer over potassium hydroxide and identified sometimes by absorption in cuprous chloride and sometimes by igniting the gas. The amounts evolved per gram-molecule of acid when the acid was heated alone and in the presence of sulphuric acid are given in the table below. In the latter case it was found that the residue contained trimethylsuccinic anhydride—shown by pouring the mixture on to ice and extracting with ether, the ethereal extract giving the corresponding acid, which, after twice crystallising from chloroform, melted at 149·5° [Found: C = 52·63; H = 7·59. Calc., C = 52·46; H = 7·56 per cent. Titration with $N/20$-sodium hydroxide. Found: 9·30 c.c. Calc. (dibasic), 9·45 c.c.].

Other Keto-acids Investigated.

a. *α-Ketoglutaric Acid.*—The *o*-phenylenediamine condensation product was prepared by mixing 1 gram of the acid dissolved in water and 0·8 gram of *o*-phenylenediamine hydrochloride in sodium acetate solution. A copious white precipitate formed rapidly in the cold, which was very sparingly soluble in ethyl or methyl alcohol and insoluble in benzene. Recrystallised from glacial acetic acid, it separated in small needles which began to darken at 140° and melted with decomposition at 155° (Found: N = 13·08. $C_{11}H_{10}O_3N_2$ requires N = 12·84 per cent.).

b. *αα-Dihydroxy-ββ-dimethylglutaric Acid.*—The *o*-phenylenediamine condensation product was obtained by gently heating

solutions of 1 gram of the acid in water and of 1 gram of o-phenylenediamine hydrochloride in sodium acetate. At about 60°, reaction *took place, causing the separation of an oil, which solidified on* cooling and yielded 1·2 grams of crude product. Recrystallised from dilute alcohol, it formed small prisms which melted at 237° (Found: C = 63·51; H = 5·86; N = 11·81. $C_{13}H_{14}O_3N_2$ requires C = 63·39; H = 5·73; N = 11·38 per cent.). The condensation product, which is formed by the elimination of 3 molecules of water, titrates with *N*/20-sodium hydroxide as a monobasic acid (Found: 8·45 c.c. Calc., 8·40 c.c.).

The residue obtained after heating the acid with sulphuric acid contained dimethylsuccinic anhydride, the corresponding acid being obtained in the manner described above (Found: C = 49·43; H = 7·44. Calc., C = 49·28; H = 6·92 per cent.).

c. *α-Keto-ββ-diethylglutaric Acid.*—Sufficient material was not available for the formation of a condensation product with o-phenylenediamine: the results obtained on heating are given in the table below.

Volume of CO evolved from 1 gram-molecule of acid in litres.

	Without H_2SO_4.	With H_2SO_4.
Balbiano's acid	16·1	39·9
α-Ketoglutaric acid	6·9	30·2
αα-Dihydroxy-ββ-dimethylglutaric acid	12·9	37·6
α-Keto-ββ-diethylglutaric acid	11·9	38·9

Note.—Theory for one CO = 22·3.

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of the materials used in the investigation.

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LXXVI.—*Studies in Catalysis. Part XV. Absorption Spectra of Triethylsulphonium Bromide in Various Solvents, in the Short Infra-red Region.*

By HENRY AUSTIN TAYLOR and WILLIAM CUDMORE McCULLAGH LEWIS.

THE simplest formulation of the radiation hypothesis of ordinary or thermal reactions as developed in earlier papers of this series assumes that chemical change is due to a specific frequency of radiation characteristic of the substance involved. Introducing

the concept of activation inherent in Marcelin's statistical treatment, and combining Marcelin's equation for the critical increment or energy of activation with the radiational eqnation based on the above assumption, we are led of necessity to a relation for thermal processes which is identical with that of Einstein for photochemical processes, namely, that one quantum of energy of the characteristic frequency ν involved is necessary to decompose or activate a single molecule (compare Part V, T., 1916, **109**, 796). From the numerical values of critical increments (which are obtained directly from measurements of the temperature coefficients of velocity constants), together with the above relation, it is possible to calculate the activating frequency or wave-length. Such calculations show that for the majority of reactions this lies in the short infra-red.

Hitherto no direct evidence in favour of this conclusion has been available. The present measurements were carried out to test directly the above mode of calculation, and the principle involved therein.

Experimental.

The measurements consisted of a series of determinations of the optical absorptive capacities of a number of substances in the short infra-red region. Preliminary work having shown that with the method employed (*vide infra*) it was impossible to obtain the extinction coefficients themselves with sufficient precision, stress is laid only on the exactness of location of a band head. A qualitative rather than a quantitative significance is to be attached to depth of bands exhibited in the graphs. Comparison, where possible, with the results obtained by others, notably by Coblentz ("Investigations in the Infra-red," Carnegie Institute Publications, Parts 1 to 6, 1905), showed that the location of a band was correct.

The reaction studied was the decomposition of triethylsulphonium bromide, the kinetics of which had been previously measured by von Halban (*Z. physikal. Chem.*, 1909, **67**, 129) at various temperatures and in various solvents. The reaction was found to be unimolecular, and from the temperature coefficients of the velocity constants in a given solvent the frequency of the absorbable radiation was calculated in the manner indicated above. At this calculated frequency or wave-length, an absorption band should manifest itself due to the solute, when a solution of the bromide in the solvent concerned is examined in the manner described below.

The measurements recorded in this paper were made with a Hilger infra-red spectrometer, of range $0{\cdot}5\mu$ to 10μ, using as source of illumination a Nernst glower consuming 0·9 ampere on a 110-volts circuit (battery of accumulators), the current being main-

tained constant by means of a sliding resistance. The measuring instrument used was a radiomicrometer, assembled according to the details given by H. C. Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 786). The absorption cells employed were essentially brass boxes, carrying an inlet and outlet allowing free passage of solvent, which filled the space between two quartz windows kept at a known fixed distance apart. Two such cells were mounted on a movable carrier immediately in front of the radiomicrometer slit, the carrier allowing rapid interchange of the two cells before the slit. By means of stops the cells were brought to precisely the same position for each repetition of an observation.

The method of observation was to compare the transmission of light of a given wave-length through each of the two cells of different thickness, the cells containing the solvent or solution under examination. The liquid passed continuously through each cell. The object of this renewal of the liquid was to prevent alteration in absorptive capacity due to change in temperature, an effect which was found to be of very great importance. The magnitude of the transmission was indicated by the deflexion of a beam of light reflected from a mirror attached to the thermocouple. The ratio of these transmissions gave the fractional and consequently the percentage transmission of a thickness of liquid equal to the difference in thickness of the two cells used. The percentage transmission is plotted against wave-length in the graphs appended.

The solvents examined were purified by distillation. The triethylsulphonium bromide was prepared according to the method of Masson and Kirkland (T., 1889, **55**, 135) from powdered sulphur and ethyl iodide, the resulting sulphonium iodide being converted into hydroxide with moist silver oxide, which was then neutralised with hydrobromic acid and crystallised. The crystals were purified by repeated precipitation from alcohol solution with ether, and dried over concentrated sulphuric acid. The extremely hygroscopic nature of the salt necessitated care and speed in the preparation of solutions to avoid the presence of water. The absence of water bands in the resulting curves showed its absence in the solutions used.

Each solvent was examined over the range $0{\cdot}7\mu$—$3{\cdot}6\mu$ and the transmission curve plotted. Each actual reading of the radiomicrometer deflexion was repeated from four to six times, the mean of these being taken to obtain the transmission ratio. The whole curve, in all cases of both solvent and solution, was repeated, the results being reproducible to within 1 or 2 per cent. transmission. Any results exceeding this limit were again examined throughout the complete course of the curve.

A saturated solution of the bromide was also made and examined under the same conditions as for the solvent, this curve being superimposed on the former. Any shift of the solution curve relative to the solvent curve could thus be detected.

The following table gives the approximate concentrations of the saturated solutions employed :

Solvent.	Per cent. by weight of solute.	Normality.	Solvent.	Per cent. by weight of solute.	Normality.
Nitrobenzene ...	0·4	*N*/50	Benzyl alcohol ...	2·6	*N*/8
Tetrachloroethane	1·6	*N*/12	Acetic acid	1·0	*N*/20
Propyl alcohol ...	0·9	*N*/22	Acetone	0·5	*N*/40
Amyl alcohol ...	1·0	*N*/20	Chloroform	1·1	*N*/18

The small concentrations of the solutions employed, rendered unnecessary any correction for the net thickness of solvent in the case of the solution, and comparison of the two curves was direct. The agreement between the two curves from about 2μ onwards would confirm this. Further, since the velocity of the reaction at the ordinary temperature is exceedingly small, no appreciable decomposition occurs during the time of examination of the solution. In case any might have occurred, an examination of a solution of ethyl bromide (10 per cent. by volume) in nitrobenzene was made, the only effect being a slight shift of the 3·25μ band of nitrobenzene towards 3·4μ. Since the concentration of ethyl bromide or diethyl sulphide, resulting from the decomposition of the triethylsulphonium bromide, in no case amounted to 10 per cent. by volume, the effect of decomposition on the solution curve could be neglected. This was further confirmed by examining the solution of triethylsulphonium bromide in nitrobenzene after complete decomposition had occurred, when it was found that the curve had become identical with that of the pure solvent. The detailed results for each solvent are given below.

Nitrobenzene.—The critical increment calculated from von Halban's data is found to be 28,390 calories, corresponding with a frequency 3·00 × 10^{14} or a wave-length 1·0μ. The accompanying graph (Fig. 1) gives the solvent and solution curves (the latter dotted). Only one distinct band due to the solute in the range examined is seen, namely, at 1·05μ, agreeing with the calculated value. The remaining slight inequalities in the two curves may be due to experimental error, the maximum difference being less than one per cent. Although the band is not a deep one, the deviation from the solvent transmission is well beyond experimental error.

Tetrachloroethane.—The calculated critical increment of 31,030 calories corresponds with a wave-length 0·91μ, which is in agreement

with that shown, where the bromide exhibits a band at $0{\cdot}90\mu$ (Fig. 2).

FIG. 1. *Nitrobenzene. Net thickness of layer* 0·2686 *cm.*

FIG. 2. *Tetrachloroethane. Net thickness of layer* 0·2686 *cm.*

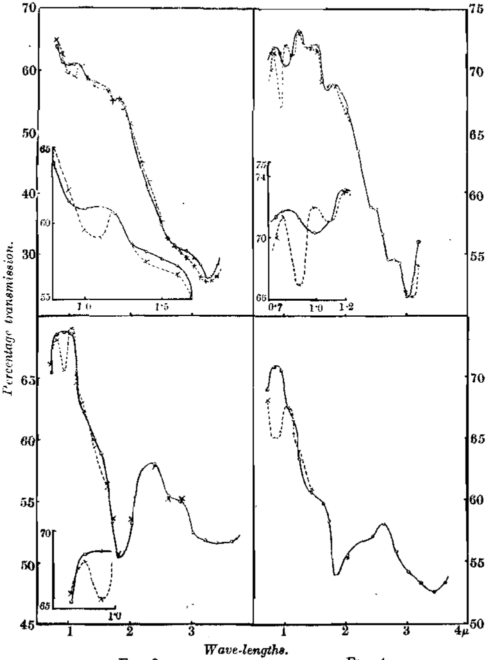

FIG. 3. *Propyl alcohol. Net thickness of layer* 0·0667 *cm.*

FIG. 4. *Amyl alcohol. Net thickness of layer* 0·0667 *cm.*

Propyl Alcohol.—The curves again show only one distinct band, namely, at $0{\cdot}89\mu$. The velocity constant data yield a critical

increment of 33,960 calories or a wave-length 0·84μ of the absorbed radiation (Fig. 3).

Amyl Alcohol.—The reaction resembles that in the previous case and yields similar resnlts. The critical increment is 33,530 calories corresponding with a wave-length 0·85μ. The agreement with the observed band at 0·83μ (Fig. 4) is closer than in the previous case.

Benzyl Alcohol.—Benzyl alcohol itself is interesting as a study of the combined effects of benzene and the paraffin alcohol groupings. The smallness of the 3·25μ, the typical benzene band, is remarkable. In the solution curve, a new band is seen at 0·80μ, which again is in agreement with the calculated position at 0·78μ obtained from a critical increment of 36,180 calories (Fig. 5).*

Acetic Acid.—The extreme opacity of glacial acetic acid together with the necessity of maintaining the room temperature above normal in order to keep the acid in the liquid state during the time of the experiment (a condition which involved some fluctuation in temperature), renders the results less trustworthy than in the previous cases. The actual magnitude of the deflexions obtained through the solvent and solntion respectively leaves no doubt, however, of the existence of increased absorption in the 0·9μ—0·95μ region in the case of the solution as compared with that of the solvent. Von Halban's data yield a critical increment of 29,220 calories, which corresponds with a wave-length of 0·97μ. The observed band with its head at 0·93μ approximately is in reasonably good agreement with that calculated (Fig. 6).

Acetone.—It is evident from the graph (Fig. 7) that in acetone the triethylsulphonium bromide exhibits a definite band at 1·3μ, a considerably longer wave-length than that observed in previous cases. It is significant that von Halban found that in acetone the bromide is ionised. The effect of this ionisation is reflected in von Halban's velocity constants, which are far from exhibiting the degree of constancy obtained in the previous cases. Owing to lack of data, von Halban was unable to correct his results satisfactorily. An attempt made by him to utilise the degrees of ionisation recorded for triethylsulphonium chloride proved ineffectual, as the constants now rose in value as the reaction proceeded, whereas previously they had fallen.

On calculating the critical increment from the kinetic data, a value is obtained which, apart from its inexactness, is necessarily

* The above result is confirmed by measurements carried out in this laboratory by Mr. A. Q. McParland, using a photographic method involving plates stained with dicyanine, in which it is found that the two lines of the copper arc at 809$\mu\mu$ are unabsorbed by benzyl alcohol, but are absorbed by the solution of the bromide.

complex, in that it involves the heat of ionisation as well as the true energy of activation of the undissociated molecule, and consequently

Fig. 5.
Benzyl alcohol. Net thickness of layer 0·2686 *cm.*

Fig. 6.
Acetic acid. Net thickness of layer 0·0017 *cm.*

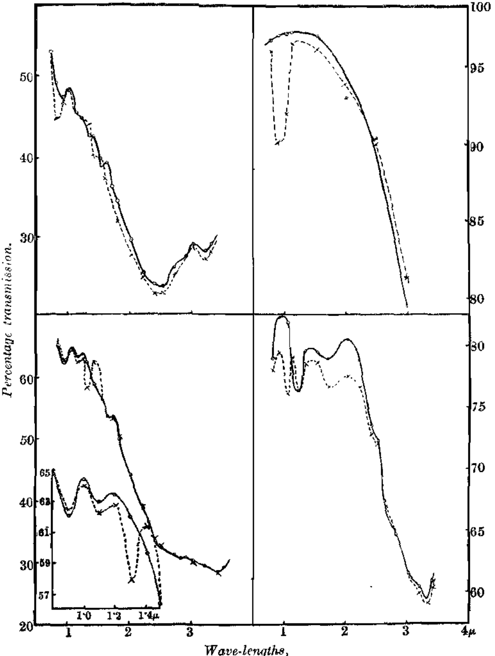

Fig. 7.
Acetone. Net thickness of layer 0·2686 *cm.*

Fig. 8.
Chloroform. Net thickness of layer 0·2686 *cm.*

a composite value such as this could not be expected to agree with the actual position found spectroscopically.

Considering the uncorrected velocity constants, that is, those which fall as the reaction proceeds, and making use of the earliest values only, the critical increment is found to be 30,450 calories between 30° and 50°, and 28,560 calories between 50° and 60°, giving a mean wave-length of about 0·96μ, which differs markedly from the observed band at 1·3μ.

Instead of comparing the velocity constants at the early stages of the reaction, it may be more justifiable to consider only those values towards the close, where the total concentration of the solute may be identified with the concentration of either ion, since the dilution is very great, and the known behaviour of the chloride indicates large ionisation. Assuming that under these conditions the electrolyte approximately obeys the law of mass action, it can be shown that:

$$E_{\text{obs.}} = E_{\text{true}} - Q,$$

where $E_{\text{obs.}}$ is the value from the final constants given by von Halban, E_{true} is the critical increment which the undissociated form itself possesses, and Q is the heat effect of the ionisation process.

The critical increment corresponding with a wave-length 1·3μ, that is E_{true}, would have a value of 21,810 calories. The difference between this value and that calculated from the final readings of the velocity data, namely, 29,540 calories, is 7730 calories evolved, which, if data were available, could be compared with the heat of ionisation of the bromide in acetone.

Chloroform.—In chloroform, the bromide has apparently created a band at 1·0μ accompanied by a range from 1·4μ to 2·2μ in which there is increased absorption but no change in the definite location of the head of the solvent band at 1·7μ (Fig. 8). In this respect, the results are distinctly different from those considered previously. As in acetone, von Halban encountered anomalous behaviour. This behaviour he suggests as being due to the fact that the bromide is polymerised in chloroform solution. The actual velocity constants which von Halban gives do not even exhibit any definite trend. The results of two investigations at the same temperature, using chloroform purified by different means, show little or no concordance. In one case, the velocity constants rise as the reaction proceeds; in the other, they first fall and then rise.

Attempting, however, to calculate a critical increment from the data by making use of von Halban's "K" values, that is, velocity constants calculated from the initial titration and the titration after a given time, and selecting out of these values of "K" those corresponding with a late stage of the process, at which point

the concentration of the bromide is least and hence the polymerisation least, values were obtained for the critical increment between 40° and 50° of 30,740 calories, between 50° and 60°, 36,240 calories, and between 60° and 70°, 32,980 calories. These values were more concordant than those calculated from any other of the recorded data, and give as a mean 33,320 calories, corresponding with a wave-length of $0{\cdot}85\mu$, which is not in good agreement with the observed band at $1{\cdot}0\mu$.

The fact that the observed band occurs at a longer wave-length than that calculated approximately from the velocity data, suggests that the critical increment obtained on the latter basis includes a depolymerisation energy term in addition to the true critical increment of the decomposition of the unpolymerised molecules.

The problem may be treated in the following manner. Consider the polymerisation as of the type :

$$2AB \rightleftarrows (A_2B_2).$$

For the equilibrium of the reaction we have

$$K = \frac{[A_2B_2]}{[AB]^2} \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

where K is the equilibrium constant. Von Halban, in calculating velocity constants, virtually writes :

rate of decomposition $= k_{\mathrm{H}} \times$ conc. of total substance,

where k_{H} is von Halban's velocity constant. The true rate of decomposition should, however, be given by $k \times [AB]$, where k is a true constant and is related to k_{H} by the expression :

$$k \times [AB] = k_{\mathrm{H}} \times \text{conc. of total substance.}$$

Assuming that polymerisation is great, the concentration of total substance is practically $2[A_2B_2]$, whence :

$$k[AB] = k_{\mathrm{H}} \,.\, 2[A_2B_2],$$

and from (1) $k = 2k_{H}\sqrt{K} \,.\, \sqrt{[A_2B_2]}$ . . . . . . (2)

In passing, it may be noticed that as the reaction proceeds the concentration of the polymerides will fall, and hence von Halban's constant should rise. His results on the whole do show this rise.

Taking logs. of (2) and differentiating with respect to temperature, we obtain :

$$\frac{d \log k}{dT} = \frac{1}{2}\frac{d \log K}{dT} + \frac{d \log k_{\mathrm{H}}}{dT} + \frac{1}{2}\frac{d \log [\mathrm{A_2B_2}]}{dT}.$$

Comparing the reaction at a series of temperatures at which the same value is given to $[A_2B_2]$, it follows that

$$E_0/RT^2 = (1/2)Q/RT^2 + E_H/RT^2,$$

where E_0 is the critical increment of the unpolymerised molecules. It follows that:

$$(1/2)Q = E_0 - E_H.$$

Experience shows that, in general, polymerisation is accompanied by an evolution of heat, that is, negative heat absorbed. Hence E_H is greater than E_0.

Assuming that the head of the observed band at $1{\cdot}0\mu$ corresponds with E_0, namely, the critical increment of the unpolymerised molecule, it follows that:

$$E_0 = 28{,}540 \text{ calories.}$$

Hence $(1/2)Q = 28{,}540 - 33{,}320 = -4780$ cals.
or $Q = 9560$ cals. *evolved* in the act of polymerisation.

The value ascribed to Q depends, however, on the correctness of E_H, which we have seen is very approximate. Also the degree of polymerisation assumed for the purpose of showing the general relation between E_0 and E_H is much less than that inferred by Turner (T., 1911, **99**, 893).

It is significant that the spectroscopic measurements do not indicate a band at $0{\cdot}85\mu$ corresponding with 33,320 calories. That is, although the polymeride is present, it is apparently incapable of decomposing directly into ethyl bromide and diethyl sulphide. Instead, it first depolymerises and then decomposes with a critical increment of 28,540 calories. The energy term 33,320 calories is therefore a composite quantity, being $E_0 - (1/2)Q$, and has no individual existence.

Concerning the increased absorption from $1{\cdot}4\mu$ to $2{\cdot}2\mu$, no satisfactory interpretation can at present be offered. The data of von Halban show that the treatment of the chloroform prior to use is sufficient to give different velocity constants, and the relative instability of chloroform itself as compared with the other solvents examined may be a factor in the abnormal behaviour observed.

General Discussion of Results.

Of the eight solvents here studied, six have been found to give results which are in good agreement with what would be expected on the basis of the simplest formulation of the radiation hypothesis, namely, that one quantum is required to decompose a single molecule. Of the remaining two solvents, acetone and chloroform,

the fact that a difference in the observed positions of absorption has been found from what might have been expected, taken in conjunction with the unsatisfactory nature of the velocity constants themselves, is significant, suggesting that the position of absorption in the short-wave region is giving possibly more trustworthy information of the reactivity of the solute than is given by the observed velocity "constants" themselves.

Summary.

(1) Using a Hilger infra-red spectrometer and radiomicrometer, the absorption spectra of triethylsulphonium bromide have been studied in eight solvents over the range 0·7μ to 3·6μ.

(2) The critical increments of the reaction in the various solvents have been calculated from von Halban's velocity constant data. From these values in turn the positions which the absorption bands should occupy have been calculated.

(3) In the case of six out of the eight solvents examined, the agreement between the observed and calculated positions of absorption has been shown to be satisfactory. The agreement in the case of two solvents, namely, acetone and chloroform, is unsatisfactory; in which cases, however, certain abnormalities in the progress of the reaction have been pointed out by von Halban.

(4) In the case of chloroform, it is concluded that the polymerised form of the solute does not decompose directly into alkyl bromide and dialkyl sulphide, but depolymerises before decomposition becomes possible.

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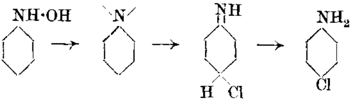
LXXVII.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part VI. The Elimination of Halogen during the Reduction of Halogenated Nitro-compounds.*

By HAROLD BURTON and JAMES KENNER.

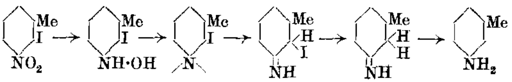
THE elimination of halogen from the benzene nucleus during the reduction of halogenated nitro-compounds has been frequently observed. Zincke and Sintenis observed that 4-bromo-*m*-dinitrobenzene was reduced to *m*-phenylenediamine by tin and hydrochloric acid (*Ber.*, 1872, **5**, 792), and 4-bromo-*m*-phenylenediamine remained unknown until Morgan employed iron filings with a little hydrochloric acid as reducing agent (T., 1900, **77**, 1202). A number

of other instances were quoted by Blanksma (*Rec. trav. chim.*, 1905, **24**, 320), who concluded that elimination of halogen occurred only when this substituent was in the ortho- or para-position to the nitro-group. Further, such elimination was facilitated by the presence of hydroxyl-, amino-, or methyl groups in the meta-position to the nitro-group. For example, 2 : 4 : 6-tribromonitrobenzene furnishes 2 : 4-dibromoaniline, but *m*-toluidine is obtained from 2 : 4 : 6-tribromo-*m*-nitrotoluene. Loring Jackson and Calvert had previously shown that 2 : 4 : 6-tribromo-*m*-phenylenediamine was converted into *m*-phenylenediamine by treatment with tin and hydrochloric acid (*Amer. Chem. J.*, 1896, **18**, 466), and Blanksma concurred in the view expressed by them that nitro-compounds of the type in question do not lose halogen until the nitro- has been converted into an amino-group.

It is obvious, however, that qualitative evidence of this character does not exclude the possibility that some halogen may be eliminated in the first stages of the reaction. Especially is this the case in view of the known reactivity of halogen in the ortho- or para-position to a nitro-group. It is also conceivable that some elimination may occur during the passage of the intermediate hydroxylamino- into the amino-compound. Thus Bamberger has explained the introduction of chlorine often observed in the course of reduction with tin and hydrochloric acid by the following scheme of reactions (*Ber.*, 1895, **28**, 201; 1898, **31**, 1504; compare also Blanksma, *Rec. trav. chim.*, 1906, **25**, 765):



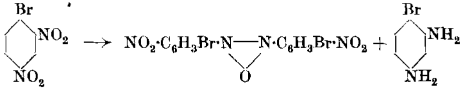
There seemed just a possibility that, during the reduction of, for example, 2-iodo-3-nitrotoluene, the following reaction might occur:



(I.) (II.)

Admittedly the product (I) corresponds with that from which *p*-chloroaniline is produced according to Bamberger's scheme, and would therefore most probably rearrange into 2-iodo-*m*-toluidine, but the possibility of its reduction in the manner indicated to (II)

needs consideration. Flürscheim and Simon, in the course of experiments on the preparation of azoxy-compounds by the acid reduction of nitro-derivatives, showed that when 4-bromo-*m*-dinitrobenzene is reduced with a small proportion of stannous chloride, no hydrochloric acid being present, ionic bromine is not produced. They therefore accepted the view of Jackson and Calvert already mentioned. But, as their product consisted of approximately 80 per cent. of azoxy-compound and 20 per cent. of amine hydrochloride (T., 1908, **93**, 1481),



it is evident that the reduction of most of the material did not pass beyond the hydroxylamino-stage, and therefore that further evidence is desirable before this possibility is definitely ruled out in the general case. It may be mentioned that in the course of the present work an experiment on somewhat similar lines, in which hydrochloric acid was employed, showed that the proportion of ionic iodine produced from 2-iodo-3-nitrotoluene was also negligible.

It appeared that more conclusive evidence on the whole matter might be gained by a quantitative comparison of the amounts of iodine eliminated from corresponding nitro-, hydroxylamino-, and amino-compounds during their reduction under conditions as closely comparable as possible. A discussion of the methods employed will be found in the experimental portion of this paper. The following table summarises the results obtained by the gradual addition of alcoholic solutions of equivalent quantities of nitro- or hydroxylamino- or amino-derivative, respectively, at a definite rate to a constant quantity of stannous chloride and hydrochloric acid at 86·5° :

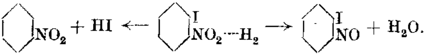
Orientation of Substituents.			Nature of Substituent X.		
Me.	I.	X.	NO_2.	NH·OH.	NH_2.
—	2	4	0	trace	trace
—	2	5	—*	8·4	12·65
—	2	3	4·9	14·8	21·5
1	3	6	9·2	11·2	13·1
1	2	5	19·5	33·6	36·1
1	4	3	21·1	42·3	—†
1	2	3	45·2	57·9	64·2

* *p*-Iodonitrobenzene was not sufficiently soluble for the purposes of these experiments.

† 4-Iodo-*m*-toluidine is described as liberating iodine on exposure to heat, or light, or air. Its "reduction" was therefore not undertaken.

The consistent increase in the values observed in each series, according as nitro-, hydroxylamino-, or amino-derivative was reduced, is at once explicable in terms of the view of Jackson and Calvert, since under the experimental conditions the proportion of reducing agent available for the removal of iodine is progressively greater in this order. The favourable influence of the methyl group in the meta-position to the nitro-group, commented on by Blanksma, is also very noticeable. Since the opposite effect is observed when the reactivity of substituents is due to an ortho-nitro-group (Kenner, T., 1914, **105**, 2717; Kenner and Parkin, T., 1920, **117**, 852), the probability is increased that the reactions now considered do not belong to this category. The results do not definitely disprove the view that halogen may be eliminated from the hydroxylamine, but this is rendered very doubtful by the outcome of an experiment with 4-iodo-5-nitro-*m*-xylene. This compound was chosen because the data already supplied indicated that a very considerable proportion of iodine would be removed during its reduction, and therefore that if this occurred to any extent prior to formation of the amino-group, the amount eliminated might be greater than the proportion of amino-compound formed, if an insufficiency of reducing agent for both reactions were employed. Actually, however, 61·1 per cent. of the total iodine was converted into the ionic form, and after allowing for this, a quantity of reducing agent remained unaccounted for, which would suffice for the formation of 61·8 per cent. of amino-compound.

Our experiments may therefore be said further to support the view that the removal of halogen in the reactions and conditions under consideration does not precede the formation of the amino-group. It has been previously pointed out that the first stage in the reduction of a nitro-group probably consists in the formation of a transitory molecular compound of hydrogen or of the reducing agent with the nitro-group (Burton and Kenner, T., 1921, **119**, 1047). According to the view advocated in this series of papers, however, the formation of such a product in the case, for example, of *o*-iodonitrobenzene represents the necessary preliminary stage to the elimination of iodine, so that the system (III) may decompose with formation either of nitrobenzene or of *o*-iodonitrosobenzene :



(III.)

The former will be facilitated by increased mobility of the halogen atom and by the use of a very mild reducing agent, corresponding with a potential difference insufficient for the electrochemical reduc-

tion of the nitro-group. Hence it is that picryl chloride may be reduced to trinitrobenzene by the action of various metals in neutral organic solvents (Meyer, D.R.-P. 234726). In general, however, the halogen is insufficiently mobile, and the reducing agent, usually stannous chloride, is too powerful. As a result, the reaction proceeds almost entirely, if not entirely, in the direction of formation of nitroso- and eventually of amino-compound. The non-elimination of halogen during the transition from the hydroxylamino- to the amino-derivative must be ascribed to the rapidity with which the product (I) assumes the aminic form, a reaction which will probably be much accelerated by the presence of strong acid.

Considering the removal of halogen from the amino-compound, it will be noted, first, that apart from hydrogen the amino-group does not render *o*-substituents reactive, and secondly, that the removal occurs in strongly acid solution and hence, in all probability, from the salt of the base rather than from the base itself. It is a confirmation of this that the preparation of such halogenated amines from the nitro-compounds is usually best achieved by the use either of ferrous sulphate and ammonia (compare, for example, Wheeler and Liddle, *Amer. Chem. J.*, 1909, **42**, 441), or of zinc and acetic acid (compare, for example, Jackson and Calvert, *loc. cit.*), or, as already mentioned, of iron and a little hydrochloric acid; in other words, under such conditions that salt-formation is largely prevented. Accepting, therefore, the view that halogen is eliminated from the salt of the base, it is then noteworthy that the effect of salt-formation on the amino-group is to confer meta-directive properties which, if perhaps not as pronounced as in the case of the nitro-group, are nevertheless quite definite. Thus, whilst the claim of Noelting and Collin (*Ber.*, 1884, **17**, 261) that the nitration of aniline in strong sulphuric acid solution results almost exclusively in the formation of *m*-nitroaniline has been shown to have been exaggerated (Hollemann, Hartogs, and van den Linden, *Ber.*, 1911, **44**, 704), it is true that the meta- and para-derivatives are formed in almost equal proportions. Vorländer, who showed that nitration of phenyltrimethylammonium nitrate, as well as bromination of the bromide, yielded a meta-derivative as sole product, also concluded that "the meta-directive influence of the ammonium group is not limited to the quaternary trimethylammonium-, but is similarly exhibited by primary, secondary, and tertiary ammonium-groups as soon as the aniline derivatives are present in strongly acid solution" (*Ber.*, 1919, **52**, [*B*], 268). This is perhaps best illustrated by the work of Tingle and Blanck * (*Amer. Chem. J.*,

* These workers also showed that it is not possible to obtain anything but dark-coloured products from the action of strong nitric acid on aniline nitrate.

1906, **36**, 605), who showed that meta-derivatives were produced by the nitration of formanilide, acetanilide, monomethyl-, dimethyl-, and diethyl-anilines respectively in sulphuric acid solution, although they were unable to confirm this in the case of benzanilide (compare Hübner, *Annalen*, 1881, **208**, 278).

The reaction in question is therefore comparable with those depending on the mobility of substituents in the ortho- or para-positions to nitro- or other meta-directive groups. When, further, it is remembered that stannous chloride has a great tendency to form the double compounds with the amine hydrochlorides which, by analogy with the view adopted in the case of nitro-groups, should represent the intermediate stage in the reactions now under discussion,

$$Ar{<}^{Hal}_{NH_2,HCl} \longrightarrow Ar{<}^{Hal}_{NH_2,HCl,SnCl_2} \longrightarrow Ar{<}^{H}_{NH_2} + SnCl_3Hal,$$

it would appear that a fairly complete basis for their comprehension has been reached, and one that may be tested by further experiment. An explanation of the influence of substituents is less easy to discover. The effect of substituents is probably the resultant of their influence in several directions. Thus, they will modify the strength of the base, and hence the completeness of salt-formation; the readiness with which the necessary additive compound of salt with stannous chloride is produced will be affected; and they will influence the mobility of the halogen atom in the manner previously discussed in this series of papers. Of these effects, the first is probably the most important, if salt-formation be fundamental to the occurrence of the reaction, and it is perhaps significant, in connexion with the favourable influence of the methyl, hydroxyl, and amino-groups in the meta-position to the amino-group, that in this position an increase in the basicity, or capacity for salt-formation, of the amino-group would be anticipated (compare Flürscheim, T., 1909, **95**, 725). Thus, *m*-toluidine is a stronger base than aniline, whereas *o*-toluidine is weaker. *p*-Toluidine is even stronger than *m*-toluidine in this respect, and therefore it will be desirable to study quantitatively the behaviour of its 3-iodo-derivative. One of us is, however, prevented from further participation in this work, and our results are therefore communicated in their present form.

Experimental.

The nitro- and amino-compounds used in the following experiments had all been previously described, with the exception of 6-*iodo*-m-*toluidine*. This base was prepared by the reduction of 2-iodo-5-nitrotoluene either by means of ferrous sulphate and

ammonia at 100°, or in glacial acetic acid solution by means of stannous chloride and hydrochloric acid. It crystallises from alcohol in colourless plates, m. p. 46° (Found: N = 6·12. C_7H_8NI requires N = 6·01 per cent.). The *hydrochloride* consists of colourless needles, and the *acetyl* derivative of colourless prisms, m. p. 147—148° (Found: N = 5·14. $C_9H_{10}ONI$ requires N = 5·09 per cent.). All efforts to obtain the base, m. p. 98—99°, described by Artmann (*Monatsh.*, 1905, **25**, 943) as resulting from the action of ferrous sulphate and ammonia on 2-iodo-5-nitrotoluene were unsuccessful.

Determination of the Proportion of Halogen Eliminated.—In the case of the nitro-compounds, the solutions for reduction were prepared by dissolving the iodonitrobenzene (10 grams), or an equivalent amount of iodonitrotoluene, in a mixture of absolute alcohol (100 c.c.) and water (10 c.c.).

The hydroxylamine solutions were prepared by reduction at the boiling point of exactly similar solutions of the nitro-derivatives in presence of ammonium chloride (0·8 gram) by gradual addition of zinc dust (14 grams) (compare Bamberger and Baudisch, *Ber.*, 1909, **42**, 3581), and filtering the colourless solutions obtained. These were then preserved from oxidation in an atmosphere of carbon dioxide.

Solutions of the amino-derivatives were made up from quantities of the bases equivalent to the above amounts of nitro-compounds, using the same quantities of alcohol and water.

The reduction experiments were carried out in a flask fitted with a cork carrying a reflux condenser, a thermometer reaching to the bottom of the flask, and a dropping-funnel. A solution of crystallised stannous chloride (23 grams, 94·6 per cent. purity) in concentrated hydrochloric acid (26·4 grams) was placed in the flask, and the whole heated to 86·5°, and maintained at this temperature by means of a water-bath. The solution for reduction was added at the rate of 5 c.c. every five minutes. Five minutes after the last addition, the solution was cooled, and made up to 500 c.c. One-tenth of this was rendered strongly alkaline with sodium hydroxide solution and extracted with ether. The aqueous solution was neutralised with sulphuric acid and treated with 10 per cent. sodium nitrite solution (10 c.c.) and dilute sulphuric acid (1·5*N*, 10 c.c.). The iodine liberated was then removed in a current of steam, and estimated by Jannasch's method (*Z. anorg. Chem.*, 1893, **1**, 144, 245) by absorption in alkaline hydrogen peroxide solution, followed by precipitation as silver iodide. It was found that unless neutralisation was performed before the treatment with nitrous acid, the precipitate contained an appreciable amount of

silver chloride. As a precaution, the silver iodide was therefore in every case washed with dilute ammonia until its weight was constant. The results obtained are shown in the table in the theoretical portion of this paper.

The conditions of reduction above described were chosen for the following reasons. The instability of the hydroxylamino-solutions renders their gradual addition to a hot solution of the reducing agent preferable to the inverse order of addition, and hence decides the mode of addition throughout. A consideration of the quantity of reducing agent to be employed at once shows that rigidly comparable experiments are not realisable, and that a compromise has to be made on this point. For very soon after the first addition of nitro- or hydroxylamino-solution has been made, amino-compound is present and is exposed to the action of the solution. For this reason it was decided not to employ quantities of stannous chloride proportional to those theoretically required for complete reduction and iodine elimination in each case, but the same quantity throughout. Further, this quantity was less than that theoretically necessary both for reduction and elimination of halogen, because this seemed to offer a greater prospect of detecting any formation of ionic iodine which might occur prior to the formation of amine. Finally, the impossibility of attaining rigidly comparable conditions of reduction seemed to render superfluous the precautions usual to ensure constancy of temperature in physico-chemical measurements.

One of us (H. B.) is glad to take the opportunity of expressing his thanks to the Department of Scientific and Industrial Research for a grant which enabled him to take part in this work. We also wish to make grateful acknowledgment of assistance from the Research Fund of the Chemical Society, and from Messrs. Whiffen and Son towards the provision of material for these experiments.

THE UNIVERSITY, SHEFFIELD. [*Received, March 2nd*, 1922.]

LXXVIII.—*The Action of Light on Silver Bromide.*

By ERNST JOHANNES HARTUNG.

THE invention of the Steele-Grant microbalance in 1909 (*Proc. Roy. Soc.*, [*A*], **82**, 580) placed a powerful weapon in the hands of investigators and, in their original memoir, the inventors expressed the hope that their instrument would prove useful in many directions. It was immediately applied by Gray and Ramsay in their brilliant researches on the atomic weights of niton and radium (*ibid.*, 1911, [*A*], **84**, 536; 1912, [*A*], **86**, 270); later, Pettersson

modified the balance and published preliminary observations on certain physical problems (*Proc. Physical Soc.*, 1920, **32**, 209). Comparatively few experimenters seem, however, to have interested themselves in the possibilities of the instrument. The vexed question of the nature of the chemical changes which take place in the haloids of silver when illuminated suggested itself as a likely subject for study, and the following pages give the results of an attempt to solve this problem by direct weighing. Unfortunately, the work was interrupted before it could be completed in all its aspects, but it was felt that the results obtained are worth recording because they throw an interesting light on the question.

The microbalance possesses important advantages for an investigation of this kind. It is capable of measuring very small differences in weight, so that one can work with very thin films of the silver compounds. It is essential that one does this, because the action of light on opaque preparations is restricted to the surface layer. Also, the balance has a very high relative sensitiveness (1 part in 10^7, or more), an important consideration when one realises that the actual weight of the silver haloid may not amount to more than one per cent. of the total load.

The instrument used in the investigation was constructed on the pattern of Steele and Grant's type-B balance. It was made entirely of vitreous silica in accordance with their directions and oscillated with a period of thirty-three seconds. It was suitably mounted in a cellar to protect it from mechanical shocks and temperature changes. The maximum load was 43 mg. and a difference in weight of 2×10^{-5} mg. could be detected. Accurate weighings to twice this quantity could be made, giving a relative sensitiveness of 1 part in 10^6. It was found that there was no need to express the results more closely than to the nearest 10^{-4} mg., and a careful sudy of the balance led to the conviction that the weighings could be absolutely depended on to this degree of precision.

Silver bromide was chosen as the first haloid for trial, and the method of experiment was very simple. Thin films of the bromide were deposited on vitreous silica supports and exposed to light under various conditions. The changes in weight were then measured. However, certain precautions were found to be necessary in order to avoid alteration in weight of the preparations from other causes. Accumulation of dust and contamination by other impurities were prevented by keeping the films always covered, by hanging them from ignited silica hooks, and by handling them on the ends of slender, ignited silica rods. There were in addition unsuspected sources of error which had to be carefully guarded against, and more particularly when working with films of metallic

silver. It was found that exposure of a silver film near vulcanised rubber resulted in steady increase in weight, although for a long time no visible change in appearance took place. This was traced to volatile sulphur compounds in the rubber, and accordingly, cork or glass stoppers were substituted with complete success in all apparatus requiring them. For the same reason, the rubber grease by which the balance case was sealed had to be made from raw, unvulcanised rubber, but even then a silver film exposed near the grease tended to gain in weight very slowly. This appeared to be due to a surface condensation of vapours given off by the material; it has been noted by other workers in the case of metallic gold and, for the present work, it was so insignificant in the balance case that it could be completely neglected.

At first it was found that silver films left hanging in the case steadily increased in weight and sometimes by as much as 0·001 mg. in twenty-four hours. This effect was traced to the condensation of mercury vapour from the manometer in connexion with the case and could be prevented by shutting the tap between the two. The presence of mercury on the silver was shown in the following way. A piece of pure silver was ignited and cut into two parts. One was introduced into a glass tube provided with a very fine capillary; the tube was then exhausted and sealed. The other was hung on the balance until any desired gain in weight had taken place, and was then sealed up in a similar exhausted tube. The two tubes were heated while the capillaries were cooled by small pieces of wet thread. Microscopic examination showed the presence of several tiny opaque globules in the second capillary, which were absent from the first one. These globules were proved to be mercury by their volatility, opacity, and metallic lustre, by their insolubility in water, and by the growth of silver crystals on them when they were immersed in an aqueous solution of silver nitrate. It was quite easy to detect in this way as small a quantity of mercury as 0·001 mg. As soon as this source of error was realised, it was a simple matter to prevent it by keeping the tap between the case and the manometer closed until a reading of the pressure was required. Fortunately also, films of silver bromide were not affected in the least.

Preparation of Silver Bromide Films.

In order to obtain very thin films of silver bromide, light vitreous silica sheets were silvered and subsequently brominated by exposure to the vapour of carefully purified bromine. At first, mica sheets were tried, but they were unsatisfactory owing to the ease with which small particles became detached and to the imprisonment of gases and liquids in cleavage cracks. The silica supports were

made by blowing bulbs and selecting suitable fragments after smashing these; the rough edges were rounded in the oxy-gas flame, and hooks attached to permit of easy handling. These supports were of course not flat; the average weight was about 40 mg. and the total surface about 5 sq. cm. They were silvered by immersion in a tartrate silvering solution and, after soaking in several changes of distilled water, were dried in an exhausted desiccator and weighed. Bromination was then effected by hanging them in the vapour of bromine purified by distillation from a mixture of bromide and bromate of potassium. The pearly-white films thus obtained weighed from 0·3 to 0·6 mg. and were almost transparent; the average thickness was about 0·2 μ. The relative amounts of silver and bromine in the film, as obtained by direct weighing, *never corresponded exactly with the proportions required* by the chemical formula of silver bromide. The halogen was always in deficit by 1 to 3 per cent. It was evident, then, that the silver deposited from the reducing solution was not quite pure, in spite of its brilliant surface and almost complete freedom from bloom; probably a small amount of occluded matter was present. In all cases it was assumed, and perhaps not entirely without justification, as later work showed, that such impurities were destroyed during bromination and that the material left on the film consisted of pure silver bromide. The same discrepancies were noticed in the preparation of films of the chloride and iodide.

It is well known that the sensitiveness of silver bromide to light depends greatly on its mode of preparation (see, for example, Weisz, *Z. physikal. Chem.*, 1906, **54**, 305). Freshly-precipitated material is more sensitive than that which has stood for some time, a change which is doubtless connected with an alteration in size of grain. The reverse phenomenon is given by the familiar ripening of emulsions for use on dry plates, but here the system is much complicated by the presence of gelatin. Unfortunately, the films prepared by brominating silver appeared to be comparatively insensitive, not only in regard to visible darkening, but also in regard to formation of a latent image rendered evident by development. Prolonged exposure to bright light was therefore required in order to obtain sufficient change for easy measurement. There was, however, the advantage that the preparations could be safely manipulated in subdued artificial light without the necessity for using ruby light on every occasion.

Action of Light on Silver Bromide in Air.

The apparatus for exposing the films to light was very simple. It consisted of a wide-mouthed glass flask of 100 c.c. capacity,

provided with two tubules through which a slow stream of filtered air could be passed. The flask was closed with a well-fitting cork stopper carrying a silica hook, from which the film hung. The apparatus was exposed on the roof of the laboratory for a definite time, a slow stream of air or other gas being maintained through the flask all the time. The changes in weight of the film were then measured. No attempt was made to estimate the intensity of the light, which varied from bright sunlight to rather dull light diffused by clouds. It was found that the films remained perfectly constant in weight in the dark, provided that they were handled carefully and shielded from such laboratory gases as the halogens and hydrogen sulphide.

The first experiments showed at once that silver bromide, when exposed to bright light, began to lose bromine with corresponding diminution of weight. This was shown repeatedly to be the case, and the following results are typical: A film of silver bromide weighing 0·3163 mg. was exposed for two hours to bright sunlight in a gentle stream of filtered air. The pale yellow colour changed to pale purple, and a loss in weight of 0·0032 mg. was recorded, which corresponds with 2·4 per cent. of the total bromine in the film. The preparation was then subjected to the action of bromine vapour in the dark; the original pale yellow colour was restored and the increase in weight was 0·0031 mg.

Experiments of this nature showed without doubt that the action of light resulted in direct loss of halogen, which could be almost completely restored by rebromination, although there was usually a slight deficiency in the amouut added on again. The actual percentage of halogen lost was always small, but could be slowly increased hy prolonged irradiation. No information as to the nature of the decomposition product on the film was, of course, obtained in this way, but it was noticed that an exposed film always left a minute, almost invisible residue on the silica after treatment with sodium thiosulphate solution. This residue weighed usually not more than 0·001 mg., and the balance was not sensitive enough to determine its nature. Although soluble in concentrated nitric acid, it was apparently not metallic silver, because the increase in weight on bromination was not sufficient to allow of the formation of silver bromide. Probably it consisted for the most part of silver sulphide, or of adsorption compounds between silver and sodium thiosulphate. It may be remarked that no residue remained when an unexposed film was treated with the sodium thiosulphate solution.

Some experiments were also performed to test the influence of water vapour on the change. Two films were exposed to the same illumination, one in a slow stream of air moistened by bubbling

through distilled water, the other in a slow stream of air dried by passing through concentrated sulphuric acid. Little difference could be detected in the rates of action in the two cases, although the experiments were not conclusive because traces of water vapour will have been present in the " dry " air. No trials were made in air subjected to the prolonged action of phosphoric oxide, but some later experiments in a vacuum indicate that the influence of moisture on the reaction cannot be great.

A few trials were made with partly brominated silver films. These had a shining black appearance with beautiful purple and green surface reflections. No change in weight could be detected after hours of exposure to bright sunlight, although there was considerable change in the appearance of the film, which became clouded with a grey bloom. It was evident that the free silver prevented loss of halogen. An attempt to discover the nature of the visible changes by trying the action of sodium thiosulphate before and after exposure failed because particles of the film became detached mechanically when it was treated with the liquid.

Action of Light on Silver Bromide in a Vacuum.

For the purpose of testing the action of light in the absence of air, the exposing vessel was modified. Glass separating flasks were employed, the stoppers and taps of which had been carefully ground. To the base of each stopper a small silica hook was attached with sealing wax; the lower portion of the vessel contained some long-fibre cotton wool kept in place by a layer of clean glass beads. After weighing, a film was hung from the hook, and the apparatus closed and thoroughly exhausted during two days in a dark room in order to remove adsorbed gases as much as possible, since heating was inadmissible. After suitable exposure, air was slowly admitted in the dark and the preparation reweighed. Re-exhaustion followed and the whole process was repeated until a practically constant final weight was obtained.

A preliminary experiment showed that in these circumstances the film darkened and lost weight very rapidly, doubtless owing to partial removal of the condensed gaseous layer on the surface of the preparation and consequent more ready diffusion of the liberated halogen away from the sphere of action. Two careful experiments were then made in a vacuum; in the first, the final result showed a loss of 80·1 per cent. of the total bromine, in the second, a loss of 86·0 per cent. of the total bromine. These losses were obtained in each case after about six days' exposure, mostly to sunshine. A third experiment was then performed, in which the air in the exposing vessel was repeatedly displaced by pure dry nitrogen

before final exhaustion. The action appeared to proceed still more rapidly in this case and, after three days' exposure, the loss in weight amounted to 84·2 per cent. of the total bromine, although this may not represent the final figure, because an accident put an end to the experiment. The films after exposure were greyish-brown; one was tested and was found to be almost completely soluble in cold, moderately concentrated nitric acid, but a careful chemical test showed that it still contained some combined bromine. The others were rebrominated; the original pale yellow colour was restored in each case, but the films were then somewhat heavier (by about 3 per cent. of the total bromine) than in the original unexposed condition. This slight excess in weight was probably due to condensation of rubber-grease vapours from the seals at the glass joints during the prolonged exposure; it will be mentioned again later.

The results of these experiments are of considerable interest, because definite conclusions as to the nature of the products of decomposition of silver bromide in light can be drawn from them. It is evident that neither oxygen nor, in all probability, water vapour is needed for the action. Consequently, the oxy-bromide theory of the darkening effect is disproved, as also is the theory which supposes that a sub-bromide is formed. From quite other evidence, Lüppo-Cramer and others have advocated the view that light action on silver haloids results in partial decomposition into metal and halogen, the metal forming solid solutions with the undecomposed haloid and so being almost insoluble in nitric acid. This view is borne out by the experiments here recorded, although, if solid solutions are formed, as indeed appears to be very likely, they are so rich in silver after prolonged exposure of thin films in a vacuum that the metal dissolves readily in nitric acid.

Silver Chloride.

A few experiments were made with silver chloride, in the same manner as those with the bromide. The films were made by submitting silvered silica films to the action of chlorine, and opalescent, almost transparent preparations were obtained. Darkening took place on exposure in air to sunlight, accompanied by loss in weight: the action appeared to proceed more easily than in the case of the bromide, a typical experiment showing a loss of 4·1 per cent. of total halogen after an exposure of three hours in the sun. This loss was almost completely restored, with the original colour, on rechlorination.

An experiment in a vacuum gave after twelve days a loss of 81·0 per cent. of the total halogen, almost all of which was shown after six days' exposure. This preparation could not be weighed

again after rechlorination owing to an accident; it was noticed, however, that the greyish-brown film darkened considerably on exposure to the halogen and then slowly assumed its original pearly whiteness. Another experiment was tried in which a film of silver chloride with another film of silver beneath it was hung and exposed for seven days in a vacuum. Such a test was recorded by Weisz (*loc. cit.*) as being originally due to R. Luther; he found that silver bromide sealed with a silver film in a vacuum darkened on exposure to light, whilst the shielded silver became tarnished. This effect was noticed in the present instance; the silver chloride darkened very rapidly and at length became greyish-brown. An iridescent layer formed at the same time on the silver, which afterwards became clouded even although it was strongly illuminated. On reweighing, however, it was found that the chloride film had lost only an amount corresponding with 23·4 per cent. of its total halogen content and the silver film had gained an amount corresponding with 57·0 per cent. of the total halogen in the system. There can be little doubt that the origin of this discrepancy must be sought in the rubber grease which sealed the stopper and tap of the apparatus. Condensation of vapours on both films would explain the results and has already been shown to take place on silver films when these are left for some time near the grease.

Silver Iodide.

Some thin films of silver iodide were made by submitting silvered silica at room temperature to the action of the vapour from carefully purified iodine. Beautiful iridescent yellow films of the iodide were soon formed. On exposure to sunlight, these films quickly lost their iridescence and then very slowly darkened. Loss in weight was again found; in a typical case, this amounted to 1·1 per cent. after three hours. The action of iodine vapour in the dark restored the original weight completely. In a vacuum, the change was much more rapid, but was still relatively slow as compared with the other haloids.

Action of Ozone on the Haloids of Silver.

It has been often stated that the action of light on the haloids of silver can be imitated by exposing them to ozone in the dark. In this way, latent images may be formed and can be rendered evident by development. Some experiments were therefore performed by exposing films of the three silver haloids for twenty hours in the dark to ozonised oxygen from an ordinary laboratory ozoniser. With silver chloride, no change in weight to 1 part in 1000 could be detected; with silver bromide, a definite loss in weight

occurred, amounting to 0·5 per cent. of the total bromine in the film, and, with silver iodide, the loss amounted to 2·8 per cent. of the total iodine. The order of these results was confirmed by repeating the experiments. On rehalogenation, the original weights were restored. It is therefore evident that there is a close analogy between the action of light and the action of ozone. The order of stability of the haloids as shown is that which might be predicted from a knowledge of the heats of formation and other characteristics of the three substances.

When exposed to sunlight in the presence of ozone, the films all lost weight more rapidly than when exposed in air alone. For example, a six hours' exposure with a chloride film showed a loss of 22·2 per cent. of the total chlorine, with silver bromide, a loss of 9·5 per cent. of the total bromine, and with silver iodide, a loss of 9·3 per cent. of the total iodine. These results show that ozone accelerates the decomposition by light, probably by oxidising the silver as soon as it is formed and in this way hindering the reverse action. The figures given do not indicate the same order of stability as those for the action of ozone in the dark, but the decomposition in light is complicated by other factors. The three haloids are differently sensitive to the various wave-lengths, the bromide reacting much more readily to blue rays than either of the others. Further, the differences in their adsorptive powers, and the differences in volatility of the halogens themselves, must exert strong influence. It may be remarked also that it is not possible to ensure by the methods used in the present work that the three films receive the same illumination, even although they may be exposed together. The want of flatness of the supporting silica films, consequent on their mode of construction, and the difficulty of ensuring that such light objects, when hanging freely, present their faces always normal to the incident illumination, make direct quantitative comparison rather uncertain. There can, however, be no doubt that the presence of ozone accelerates the decomposing action of light on silver haloids, although it is equally certain that the changes take place quite readily in the absence of oxygen.

The question now arises whether the actinic decomposition of the silver haloids can be made complete. Previous work had shown that, although the actions were reversible, yet there was great difficulty in obtaining any considerable loss of halogen, even after prolonged irradiation. The present work indicates that the reason for this behaviour is due to the opacity of the material in bulk and to the condensed layer of gases on the surface preventing free diffusion of the liberated halogen from the sphere of action. Exposure of very thin films in a vacuum removes these hindrances and decomposition is then rapid. If the concentration of the

halogen in the exposing vessel is kept negligibly small by the presence of a suitable absorbent, it should be possible to get complete decomposition. In the experiments here recorded, the rubber grease used on stoppers and taps doubtless acted as a good absorbent for the small amounts of halogen concerned, but some of the results were vitiated by the condensation of its vapours on the films. It is not quite evident why this effect should have been so pronounced in the case of the chloride and iodide experiments, although the weather was then comparatively hot and also a new sample of the grease, of rather lower melting point than the first specimen, was used. Certainty in the results can only be obtained by avoiding the use of rubber grease altogether.

Recently the question has been attacked in a different and most ingenious way by Ehlers and Koch (*Z. Physik*, 1920, **3**, 169). They suspended excessively minute particles of silver bromide between the charged plates of a condenser and measured the alteration of potential which was needed to keep the particles in position after illumination. The results obtained do not always agree with those given above; for example, a gain in weight was observed in air, and a loss in nitrogen. No criticism of this work is ventured because only an abstract of the authors' paper has been available; one would think, however, that difficulties in connexion with adsorption and variation of charge must be very great with particles of such minuteness.

Summary.

1. The microbalance has been applied to the study of the action of light on silver haloids.

2. It has been shown that thin films of the chloride, bromide, and iodide of silver lose weight when exposed in air to sunlight. This is due to loss of halogen, and the original weight is almost completely restored by rehalogenation.

3. The decomposition is greatly accelerated in a vacuum. It has been shown that silver bromide decomposes into silver and bromine.

4. Evidence is adduced to show that the chloride, and probably also the iodide, behave similarly.

5. The decomposition of the haloids is accelerated by ozone, but the presence of oxidising agents is not essential.

My sincere thanks are due to Professor Orme Masson for his kindly and critical interest in the work, and to Mr. G. A. Ampt, B.Sc., for expert advice on all matters connected with the manipulation of the microbalance.

CHEMICAL LABORATORIES,
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LXXIX.—*Purification of Phosphoric Oxide.*

By George Ingle Finch and Raymond Harold Kelsall Peto.

Even the purest samples of phosphoric oxide obtainable commercially invariably contain more or less considerable traces of impurities, consisting, for the most part, of lower oxides of phosphorus, the presence of which can be readily detected by their reducing action on solutions of silver nitrate or mercuric chloride. These lower oxides volatilise readily and are powerful catalyst poisons. It is therefore essential that phosphoric oxide, when employed as a drying agent in the experimental study of heterogeneous catalytic gas reactions, should be free from such impurities.

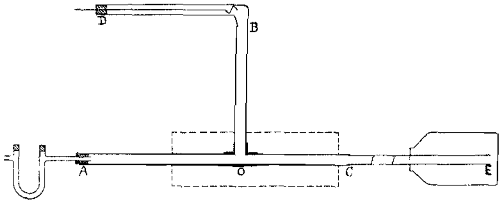
Threlfall (*Phil. Mag.*, 1893, [v], **35**, 14) prepared pure phosphoric oxide by distilling the commercial product in a current of oxygen over platinised asbestos. Shenstone and Beck (T., 1893, **63**, 475) tried Threlfall's method, but found that platinised asbestos was unsatisfactory and used instead platinum sponge. Travers (" Experimental Study of Gases," p. 41) throws commercial phosphoric oxide into a red-hot porcelain basin and stirs the mass in a current of oxygen. Baker (private communication) has found that none of these methods is satisfactory, the chief defects being the poor yields obtainable and the amount of attention required to supervise their prosecution. He distils commercial phosphoric oxide at a temperature of from 180° to 210° in a current of oxygen, but employs no catalyst. The yield is poor (about 10 per cent.), but the process, although long, requires a minimum of attention. We have compared this method with that of Shenstone and Beck, and found it greatly superior to the latter. Travers's process was also tried, a red-hot iron basin being substituted for a porcelain one; not only, however, was the yield poor, but also the product was not free from lower oxides.

As a considerable quantity of phosphoric oxide was required by us, an attempt was made to devise a more satisfactory method of purification, by means of which a better yield could be obtained more rapidly than is possible by any method hitherto employed. In the method about to be described, phosphoric oxide was sublimed at a bright red heat in a current of dry oxygen.

The apparatus consisted of an inverted T-piece, *OABC*, of stout iron pipe, a portion of which could be heated in a furnace to a bright red heat. A glass tube, *BD*, provided with a rake of iron wire and closed with a cork, fitted into the top of the vertical limb of the iron pipe at *B*. At *C*, one end of a piece of combustion tubing 4 feet long fitted into the horizontal limb of the iron pipe; the other end

entered a large glass bottle, *E*. Glass-to-iron joints were cemented with phosphoric acid and any leaks soon became choked by the escaping sublimate. The part of the iron pipe within the furnace was maintained at a bright red heat and, while a steady stream of dry oxygen from a cylinder was admitted at *A*, the impure phosphoric oxide with which the glass tube *BD* had been filled was raked down into the hot pipe a little at a time. The phosphoric oxide sublimed immediately and the sublimate was carried along in the current of oxygen into the cold tube, *CE*, where the greater part of the sublimate condensed. A small part of the pentoxide was carried into the bottle, *E*, where it served to dry the air surrounding the open end of the glass tube. The phosphoric acid present in the commercial pentoxide remained behind in the iron pipe as a molten glass.

FIG. 1.



An approximately 50 per cent. yield of purified phosphoric oxide was obtained. It was partly crystalline and partly amorphous, and was tested for lower oxides of phosphorus in the following way: 0·5 gram of the sublimate was dissolved in water and neutralised to methyl-orange with sodium hydroxide; to this was added a slight excess of a solution of silver nitrate. The solution and the white precipitate of silver phosphate were boiled together for five minutes without any change taking place in the colour of either, whereas, when the same test was applied to the original commercial phosphoric oxide, silver phosphate of a dark brown colour was produced. We had no difficulty in preparing in this way 50 grams of pure pentoxide in one hour.

In conclusion, we desire to state that one of us (R.H.K.P.) has been assisted in this work by a grant from the Department of Scientific and Industrial Research.

DEPARTMENT OF CHEMICAL TECHNOLOGY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. [*Received, March 11th*, 1922.]

LXXX.—*The 25°-Isotherms of the Systems Magnesium Nitrate–Sodium Nitrate–Water and Magnesium Sulphate–Magnesium Nitrate–Water.*

By Douglas Norman Jackman and Agnes Browne.

The quaternary system Na–Mg–NO_3–SO_4–H_2O is of interest as it occurs naturally in the Chile nitrate deposits.

Of the four ternary isotherms required for the investigation of this system two are known:

Na_2SO_4–$MgSO_4$–H_2O (Blasdale, *J. Ind. Eng. Chem.*, 1920, **12**, 164).

Na_2SO_4–$NaNO_3$–H_2O (Massink, *Z. physikal. Chem.*, 1917, **92**, 351).

No work has been published on the systems $NaNO_3$–$Mg(NO_3)_2$–H_2O and $Mg(NO_3)_2$–$MgSO_4$–H_2O. The 25°-isotherm of each was undertaken in this laboratory, the latter by Agnes Browne.

Experimental.

The sodium nitrate and magnesium sulphate used were pure analytical reagents.

The magnesium nitrate obtainable was found to contain a small amount of sulphate. This was removed by the cautious addition of barium hydroxide followed by treatment of the boiling solution with carbon dioxide. The filtered liquid was allowed to crystallise and the solid twice recrystallised. The product was free from barium and sulphate.

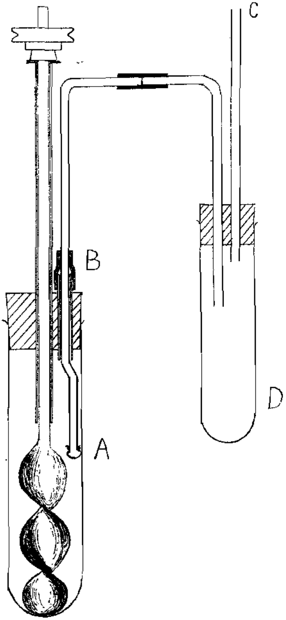
In order to obtain an isothermal separation of the solid and liquid phases, the apparatus shown in Fig. 1 was employed.

The only points requiring explanation are the filter, *A*, and the loose but water-tight joint, *B*, which consists of a sleeve of rubber tube. The filter is composed of two layers of fine linen fastened over the widened end of the filter tube with a rubber ring. Quantities of the two salts and water were introduced into the left-hand tube in proportions to give approximately the required phases. The tube was then closed and its contents were stirred in the thermostat at 25° ± 0·1° for twelve to twenty-four hours. It was found desirable slightly to warm the mixture before placing it in the thermostat. The filter-tube, *A*, was raised during stirring and lowered to the bottom as soon as stirring ceased. The solid phase then collected above the filter so that gentle suction through *C* caused the collection of the liquid phase in *D*, leaving a moderately dry "rest." The whole apparatus was then removed from the thermostat, and the tubes were dried, disconnected, and stoppered.

They were then weighed, the whole of each phase was dissolved in water, the solutions were diluted to 250 c.c., and 25 c.c. were employed for each estimation.

Analysis.—(1) The system $NaNO_3$–$Mg(NO_3)_2$–H_2O. Magnesium was estimated as pyrophosphate. Direct estimation of sodium being very troublesome, this method was employed only to locate the last three points on the diagram, where a "difference" method would be liable to show considerable errors on account of the small amounts of sodium present. For the estimation of sodium by difference, the total nitrate was estimated by reduction with Devarda's alloy. It was found necessary to add the strong solutions of potassium hydroxide slowly from a tap-funnel in order to avoid alkaline fog being carried over during a rapid evolution of hydrogen. *An analysis* of the pure sodium nitrate gave 0·561 gram taken; 0·563 gram found. A blank experiment showed that no alkali was carried over from the materials used into the receiver.

FIG. 1.



For the direct estimation of sodium, the following method was employed: 50 c.c. of the solution were evaporated in a platinum dish, and the residue was dried and ignited to decompose magnesium nitrate. The residue was extracted several times with water to remove the sodium salt. The magnesium oxide was dissolved in strong nitric acid, and the solution evaporated, ignited, etc., as before; the aqueous extract was added to the previous ones. The combined extracts were evaporated to dryness

twice with concentrated hydrochloric acid, and the sodium chloride formed was titrated with silver nitrate solution.

(2) The system $MgSO_4$–$Mg(NO_3)_2$–H_2O. Magnesium and sulphate were estimated in the usual way and the nitrate was obtained by difference.

Results.—The following tables give the percentage composition of the liquid phases and some of the corresponding "rests." It was not considered necessary to analyse all the intermediate "rests."

TABLE I.

$Mg(NO_3)_2$–$NaNO_3$–H_2O.

Liquid.			"Rest."			Solid phase.
$Mg(NO_3)_2$.	$NaNO_3$.	H_2O.	$Mg(NO_3)_2$.	$NaNO_3$.	H_2O.	
—	47·60	52·40				
4·35	42·56	53·09	—	—	—	
9·82	36·58	53·60	3·81	78·08	18·11	
12·60	32·93	54·47	—	—	—	
16·12	28·39	55·49	—	—	—	$NaNO_3$.
25·25	18·26	56·49	—	—	—	
26·90	17·00	56·10	—	—	—	
34·24	11·10	54·66	12·20	69·70	18·10	
36·98	9·70	53·32	11·70	72·00	16·30	
38·25	9·22	52·53	39·70	30·60	29·70	$NaNO_3$ + $Mg(NO_3)_2,6H_2O$.
40·00	5·12	54·88	45·54	3·35	51·11	
40·84	3·37	55·79	49·40	1·80	48·80	$Mg(NO_3)_2,6H_2O$.
43·25	—	56·75				

FIG. 2.

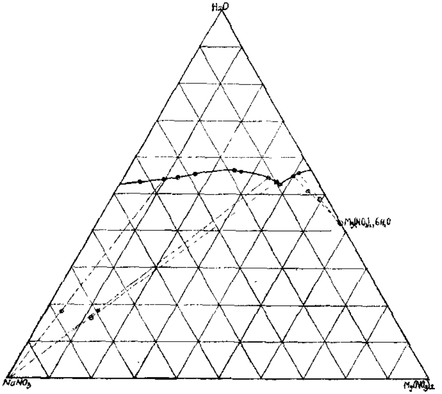
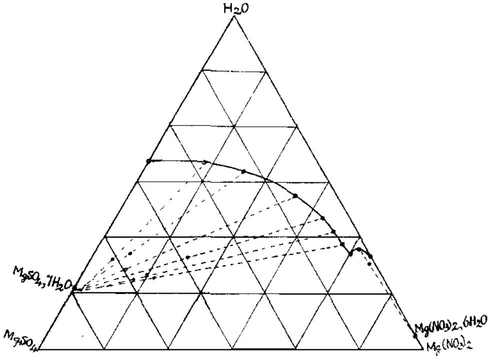


TABLE II.

$Mg(NO_3)_2$–$MgSO_4$–H_2O.

Liquid.			"Rest."			Solid phase.
$Mg(NO_3)_2$.	$MgSO_4$.	H_2O.	$Mg(NO_3)_2$.	$MgSO_4$.	H_2O.	
—	26·30	73·70				$MgSO_4,7H_2O$.
8·88	17·85	73·27	3·42	40·70	55·88	$MgSO_4,7H_2O$.
15·56	12·53	71·91	5·44	37·53	57·03	$MgSO_4,7H_2O$.
25·90	6·56	67·54	6·24	39·49	54·27	$MgSO_4,7H_2O$.
32·22	4·18	63·60	14·84	28·73	56·43	$MgSO_4,7H_2O$.
35·07	3·62	61·31	8·54	39·27	47·81	$MgSO_4,7H_2O$.
37·75	3·09	59·16	11·46	35·96	52·58	$MgSO_4,7H_2O$.
40·15	2·77	57·08	41·13	6·56	52·31	$MgSO_4,7H_2O$ + $Mg(NO_3)_2,6H_2O$.
40·76	1·02	58·22	43·75	0·77	55·48	$Mg(NO_3)_2,6H_2O$.
43·25	—	56·75				$Mg(NO_3)_2,6H_2O$.

FIG. 3.



Summary.

It has been shown that in these two systems no double salts or solid solutions are formed at 25°.

Our thanks are due to Professor F. G. Donnan, F.R.S., for suggesting this investigation.

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GOWER STREET, LONDON, W.C. 1. [*Received, March 7th*, 1922.]

LXXXI.—*The Decomposition of Ammonium Nitrate by Heat.*

By HORACE LEONARD SAUNDERS.

THIS research was undertaken owing to the many reports regarding the manner in which ammonium nitrate decomposes when heated. These reports agree in giving the main course of the reaction as $NH_4NO_3 \longrightarrow N_2O + 2H_2O$, but nitric oxide, nitrogen peroxide, free ammonia, and free nitric acid have also been found. Measurements are given only in one instance, where the reaction was carried out at a red heat (Favre and Silbermann, *Ann. chim. phys.*, 1852, [iii], **36**). It is well known that if ammonium nitrate is too strongly heated when used for preparing nitrous oxide, red fumes are produced, and soon will follow a rather violent explosion. Hence there must be some change in the nature of the reaction at this point, either with regard to time or temperature. If the nitrate should contain small quantities of chlorides, the gas evolved invariably contains chlorine. The problem thus becomes :

1. To ascertain the nature of the decomposition of pure ammonium nitrate at moderate temperatures.
2. To ascertain how the presence of small quantities of commonly occurring impurities modifies this decomposition.
3. To ascertain the nature of the explosive decomposition.

The method selected for estimating the nitrous oxide was explosion with excess of hydrogen.

Ammonium nitrate of commerce is liable to contain chlorides and sulphates of ammonia and sodium and also sodium nitrate in quantities up to 1·5 per cent. Therefore the influence of each impurity must be investigated. The first part of this research was directed to the decomposition of the specially purified nitrate. It was dried at 100° for two days and reduced to a fine powder. In all the experiments, unless otherwise stated, 40 grams of material were used.

Outline of the Method.

The ammonium nitrate is heated in a large tube, *H* (Fig. 1), which is placed in a thermostat, containing an oil of high boiling point, the temperature of which is given by the thermometer, *D*. Stirring is effected by the automatic fan, *E*, and the mill wheel, *G*. The temperature of the nitrate is given by a second thermometer, *J*, the bulb of which is immersed in the molten mixture. The products of the reaction are led away to a condensing tube, *L*, where an acid liquid collects, which may be drawn off by turning the tap. From here the gas passes on to *M* or *N*, as may be necessary. *N* contains

sodium hydroxide to absorb acid vapours or chlorine (p. 703). After this, the gas is collected over mercury in the vessel, *O*. This gas may now be submitted to analysis in the Haldane apparatus. The hydrogen required in these experiments is passed into the burette, *Y*, which contains alkaline pyrogallol to absorb traces of

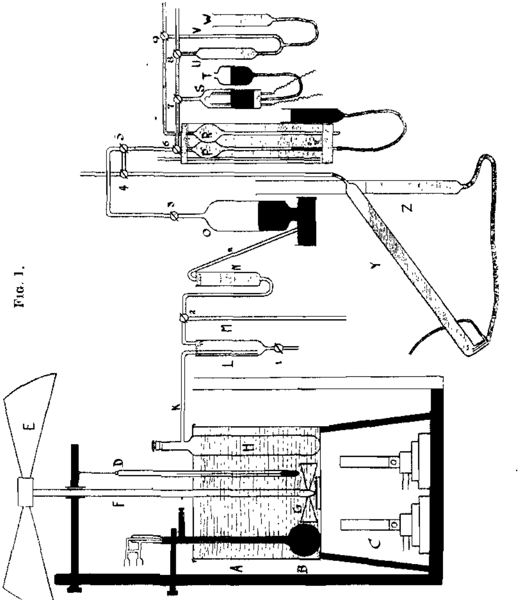


Fig. 1.

diffused oxygen. Further, the rubber joints through which the hydrogen passes are varnished with shellac to minimise diffusion. Haldane's apparatus is slightly modified; the stem of *P* is graduated in 1/100 c.c., the explosion chamber is made double the usual size, and a new form of spark gap substituted, where one electrode forms an arc at the centre of which the other is situated. (When

the ordinary form was used, some of the explosions were very violent, often shattering the tube.)

By suitably turning the taps 3, 5, 6, a sample of the gas is drawn over into *P* and measured, the liquid in the compensating tube being meanwhile adjusted to the mark on *V*. The gas is passed to the explosion chamber *S*, which was previously full of mercury, and the tap 7 closed. The capillary tubes from 5 onwards are washed out by drawing hydrogen through them, and then filled again with mercury. By turning taps 4, 5, 6, hydrogen is admitted into *P*, and its volume measured as before. It is then passed into *S*, and mixing effected by passing the gases from *S* to *P* and back again five times. The tap 7 is closed, the pressure reduced, and the mixture exploded by a spark from an induction coil. After the lapse of a few minutes to allow for cooling, the gases are passed back into *P* and measured. The level in *V* should remain undisturbed when this tube is again put in communication with *R*; if this is not the case, a correction may be applied up to 0·5 per cent. or the experiment is repeated. The proportion of hydrogen used is adjusted so that it is always just in excess of that required; a large excess limits the completeness of the reaction.

All the preliminary experiments were made in the above apparatus, including the series in which rises of temperature were measured (chloride mixtures, p. 705). In order to obtain satisfactory results, it was found that there must be no cork or rubber at any place where heated products of the reaction must pass. Thus the tubes *H*, *K*, *L* were fused together, and *H* was fitted with a ground-glass stopper to facilitate the introduction of the nitrate.

The gases were tested for nitrous oxide, nitric oxide, nitrogen peroxide, ammonia, nitrogen, and oxygen, the last alone being invariably absent. Samples of the gas evolved at 240° were passed through ferrous sulphate solution for half an hour, but no colour change was observed; hence the quantity of nitric oxide must have been very small. Any nitrogen peroxide will have been absorbed in the sodium hydroxide in *N*, but the amount was very minute. The nitrous oxide was found as stated above, and the free nitrogen given by difference. The estimation of the nitric oxide and nitrogen peroxide was carried out in the following way: the sodium hydroxide tube was removed and the gases were passed through an acidified solution of potassium iodide, the volume of the gas being afterwards measured. The liberated iodine was titrated with thiosulphate, and the volume of nitrogen peroxide corresponding with the iodine calculated. The nitric oxide and nitrogen peroxide were then estimated together. A known volume of the gas was collected over mercury, and a few

c.c. of dilute potassium iodide solution were introduced into the gas, which was then shaken. Owing to the solubility of the nitrous oxide, a slight vacuum was produced, and air was then admitted so that the nitric oxide was oxidised, and liberated iodine. This process was repeated several times, and the iodine titrated as before. *The nitric oxide was then found by difference. The results are* given in Tables I and II.

TABLE I.

Nitrogen peroxide.		Nitric oxide.		
C.c. of gas taken.	Nitrogen peroxide. Per cent.	C.c. of gas taken.	$(NO_2 + NO)$. Per cent.	Nitric oxide. Per cent.
500	0·001	100	0·0024	0·001
,,	,,	,,	0·0022	,,
,,	,,	,,	0·0024	,,
,,	,,	200	0·0023	,,
,,	,,	,,	0·0024	,,

The following results show a series of time reactions, readings being taken half-hourly after the apparatus was free from air.

TABLE II.

Percentage of nitrous oxide in the gas evolved from the pure nitrate.

Temp.	Vol. of gas.*	Vol. of hydrogen.*	Contraction.	Nitrous oxide. Per cent.
233°	712	867	794	97·5
	703	790	683	97·2
	726	781	707	97·4
	732	882	717	98·0
	715	904	700	98
	710	766	693	97·7
	722	908	708	98·1
	706	923	694	98·3
220°	712	918	695	97·6
	715	850	697	97·5
	709	901	693	97·7
	713	923	699	98·1
	705	784	686	97·3
	717	831	700	97·6
	743	857	729	98·1
	720	857	707	98·2
	705	896	691	98·1
234°	724	918	704	97·3
	721	912	706	98
	700	912	682	97·4
	712	923	695	97·6
	715	912	700	98
262°	718	973	706	98·3
	727	916	716	98·5
	713	910	701	98·3
	720	902	708	98·3
	720	965	705	98
	718	953	702	97·8
	738	980	723	97·9

* In hundredths of a c.c.

Decomposition of the Pure Nitrate [up to 260°].

Pure dry ammonium nitrate decomposes only slowly at 200°, liberating 20 c.c. of gas per 50 grams of nitrate per hour. The nitrate first melts at 169°, then dissociates into nitric acid and ammonia, and begins to evolve a gas containing 98 per cent. of nitrous oxide. Free nitrogen is always present; the quantity is nearly 2 per cent. up to 260° and considerably exceeds this at higher temperatures (see p. 710). Nitrogen peroxide and nitric oxide are also present, the average amount between 220° and 260° being 0·001 per cent. of each.

The liquid products of the reaction contain nitric and nitrous acids and a small quantity of ammonium nitrate, which, being volatile, is carried over with the gas.

There is evidence that, after dissociation, the action between the ammonia and nitric acid proceeds even in the condensing tube; a glass rod held at the mouth of the heating tube is quickly coated with a deposit of nitrate, whereas in the condensing tube only a trace of ammonia is found.

The following equations represent the course of the decomposition :

1. $NH_4NO_3 \rightleftarrows NH_3 + HNO_3$
2. $NH_4NO_3 \rightarrow N_2O + 2H_2O$
3. $5NH_3 + 3HNO_3 \rightarrow 9H_2O + 4N_2$,

the second denoting the main change. In support of the third we have the fact that the liquid which collects is always acid, showing that an excess of ammonia is used up in the reaction; also free nitrogen is always present.

The rate of evolution of gas increases with rise of temperature and up to 250° is steady. Above this point, the gas is often evolved in rushes, and in two instances a slight explosion took place just above 260°. The experiments were therefore not carried further in this form of apparatus.

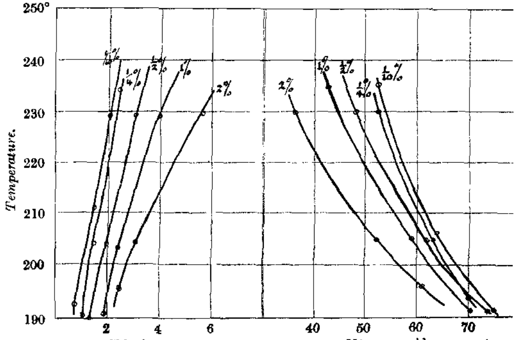
The Influence of Impurities.

(*a*) *Chlorides.*—The commonest impurities in commercial ammonium nitrate are the chlorides of ammonia and sodium. In order to study the modifying influence of these substances, a series of mixtures was made containing quantities of chloride ranging from 0·1 to 2 per cent. In all cases the "impurity" was specially purified by recrystallisation. A known quantity of the mixture is introduced into the tube *H*. The temperature of the thermostat having been adjusted, the tube is inserted, and the gases are collected in the ordinary manner. The tube *L* acts as a condenser,

and the gases, after passing this, flow through the tube containing sodium hydroxide, where chlorine is absorbed. The surface of the mercury in *O* is covered with a layer of sodium hydroxide solution to ensure complete absorption of chlorine. The remaining gases are then submitted to analysis as before. In order to make measurements of the quantity of chlorine present, the gas is passed through the tube *M* into a solution of potassium iodide, the remaining gas being collected over mercury and its volume measured. The percentage of chlorine may then be calculated.

FIG. 2.

Graph showing composition of gas when ammonium chloride is present.



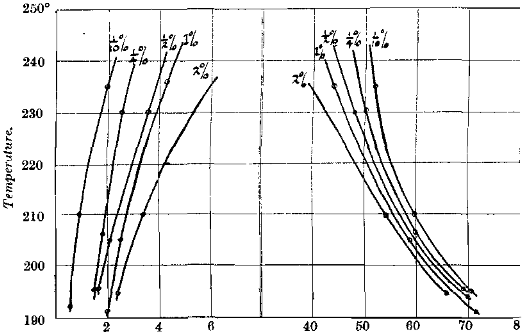
These experiments were conducted as before in two complete series: in the first, general observations were made and rises of temperature noted; in the second, where the joints were glass sealed, the final readings were taken. The reason for making the two series is as follows. When the temperature of the mixture is gradually raised until the reaction sets in, there is a sudden evolution of gas which contains chlorine; then the action suddenly slows down. On account of the rush of gas at first obtained, it was thought that there might be an initial rise of temperature and on introducing a second thermometer into the reacting mixture this was found to be the case. This rise depends on the quantity of the reacting substances and the temperature of the thermostat. It was therefore not possible to keep the temperature actually

constant, and the following method was adopted—the thermostat was set to a definite temperature, and by means of a second thermometer the initial rise was measured. Once this preliminary reaction was at an end, the temperature gradually fell to that of the thermostat. The initial reaction was usually completed in from five to thirty minutes. Table III gives the rises (the differences of columns 2 and 3) and induction periods for various mixtures.

An examination of the relative amounts of chloride in the original and final mixtures from which the gas was being evolved showed

FIG. 3.

Graph showing composition of gas when sodium chloride is present.



that the chloride was decomposed faster than the nitrate. Hence it might be expected that the final composition of the gas would be the same as that evolved from the pure nitrate, provided that the heating were continued long enough.

Five sets of experiments were made, using 0·1, 0·25, 0·5, 1, and 2 per cent. of chloride respectively. These were conducted at different temperatures, and in each case measurements were made of the quantity of nitrous oxide, chlorine, and nitrogen in the gas evolved during the preliminary reaction. The results are shown in tables IV and V and illustrated in Figs. 2 and 3. According to the above experiments, the actual temperature of the molten mixture was some 10° to 20° higher than that here represented.

This rise was a somewhat variable quantity, depending on the mass and other factors. Therefore the same weight of material was used on each occasion and the temperature of the thermostat taken as the basis of calculation.

The modifying influence of sulphates and sodium nitrate was next investigated.

TABLE III.

Impurity per cent.	Temp. of the thermostat.	Temp. of the mixture.	Period of induction.	Impurity per cent.	Temp. of the thermostat.	Temp. of the mixture.	Period of induction.
0·1 NH_4Cl	215°	224°	—	0·1 NaCl	210°	222°	—
	,,	226	—		,,	219	—
0·25 ,,	193	—	1 hr. 20 m.	0·25 ,,	,,	218	15 min.
	205	222	—	0·5 ,,	,,	223	—
0·5 ,,	215	236	10 min.	1 ,,	200	214	20 ,,
	185	198	25 ,,		,,	213	20 ,,
	205	222	5 ,,	2 ,,	210	233	30 ,,
1 ,,	,,	225	8 ,,		230	260	1 ,,
	200	211	15 ,,	1 $(NH_4)_2SO_4$	210	221	10 ,,
	,,	215	15 ,,	2 ,,	,,	215	20 ,,
2 ,,	,,	218	27 ,,		220	225	—

TABLE IV.

Table showing the variation of the amount of chlorine in the gas with different percentage admixtures of impurity and with temperature.

Temp.	Impurity per cent.	Chlorine per cent.	Temp.	Impurity per cent.	Chlorine per cent.
192°	0·1 NaCl	0·6	193°	0·1 NH_4Cl	0·8
212	,,	0·96	212	,,	1·5
235	,,	1·9	230	,,	2·2
196	0·25	1·6	190	0·25	1·2
206	,,	1·9	203	,,	1·5
234	,,	2·7	235	,,	2·2
194	0·5	1·6	190	0·5	1·3
205	,,	2·2	205	,,	2·0
230	,,	3·85	230	,,	3·1
191	1	2·0	191	1	—
205	,,	2·5	205	,,	2·45
236	,,	3·6	235	,,	4·1
195	2	2·4	196	2	2·35
210	,,	3·5	205	,,	3·1
230	,,	—	230	,,	5·75

General Nature of the Results obtained with Chloride Mixtures.—It is difficult to state definitely the temperature at which the decomposition commences. Taking as a typical example the behaviour of 50 grams of a mixture containing 1 per cent. of ammonium chloride, the reaction sets in at 199° if the temperature

TABLE V.

Table showing the composition of the gas (by averages) with relation to temperature.

Impurity per cent.	Ammonium chloride. Temp.	Cl_2.	N_2O.	N_2.	Sodium chloride. Temp.	Cl_2.	N_2O.	N_2.
0·1	193°	0·8	70·0	29·2	192°	0·6	70·6	28·8
	212	1·5	59·9	38·6	210	0·95	59·0	40·05
	230	2·2	53·3	44·5	235	1·9	52·8	45·4
0·25	190	1·2	75·5	23·3	196	1·6	69·4	29·0
	205	1·5	64·2	34·3	206	1·9	59·8	38·3
	235	1·75	52·4	45·4	230	2·7	50·5	46·8
0·5	190	1·3	73·8	24·9	194	1·6	71·2	27·2
	205	2·0	62·2	35·8	205	2·2	59·8	38·0
	230	3·1	48·5	48·4	230	3·6	47·8	48·6
1	191	1·9	70·0	28·1	191	2·0	71·6	26·4
	205	2·45	59·0	38·55	205	2·6	59·0	39·4
	235	4·1	43·3	52·6	236	3·8	43·3	52·9
2	196	2·4	61·0	36·6	195	2·4	65·4	32·2
	205	3·1	52·2	44·7	210	3·4	54·4	42·2
	230	5·75	37·0	57·25				

The graphs are constructed from these tables.

is raised directly. If the same mixture is kept at 180°, the action will start after one and a quarter hours; and the temperature may now be lowered to 175° without causing it to stop completely. At 210°, the decomposition is not unduly rapid, but at higher temperatures the mixture froths violently and is carried over by the rush of gas.

When any mixture is raised to a particular temperature there is at first a passive period, varying from a few minutes to one and a half hours (Table III), depending on the amount of impurity present, on the temperature, and possibly on the presence of free nitric acid (compare Veley, *Chem. News*, 1883, **41**, 299). Then a new reaction sets in, chlorine is evolved, and in some cases the amount of nitrous oxide falls by 50 per cent., whilst the percentage of nitrogen increases. This is accompanied by a marked rise of temperature, and directly this has attained a maximum the flow of gas suddenly slackens. During the first period the composition of the gas remains constant for any particular mixture, but as soon as the temperature begins to fall, most of the chloride having decomposed, the composition of the gas gradually approximates to that given by the pure nitrate at the same temperature, the process taking several hours.

The action of the chlorides of ammonia and sodium is very similar, that of the former being the more marked. In all cases the amount of chlorine present depends on the amount of impurity

and on the temperature. The action of the chloride is certainly catalytic in character, 1 part in 1,000 being quite sufficient to alter entirely the main course of the decomposition.

Of the three reactions mentioned on p. 702, the last assumes an important part in the case of chloride mixtures, especially when the temperature rises above 215°, the chloride accelerating this reaction and not the second. Further, the acid liquid which collects in the condensing tube now contains hydrochloric acid also, and this may be formed by the interaction of chlorine and ammonia—$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$, thus accounting for the presence of some of the nitrogen. The chlorine is probably formed by the interaction of the hydrochloric and nitric acids set free by dissociation.

(*b*) *Ammonium Sulphate.*—With a 1 per cent. mixture the temperature may be raised to 200° before the action sets in, with an initial rise of 10°. The action is very sluggish, the more so as the proportion of sulphate is increased; with a 2 per cent. mixture the lowest working temperature is 215°, when the initial rise is only 5°. The gas evolved sometimes contains a trace of ammonia, but otherwise there is no change in its composition.

(*c*) *Sodium Sulphate.*—A 1 per cent. mixture does not influence the reaction between 220° and 250°.

(*d*) *Sodium Nitrate.*—Mixtures with 1 per cent. and 2 per cent. of sodium nitrate are without characteristic action.

Explosive Decomposition.

In carrying out this series of experiments, considerable modifications of both apparatus and method were found to be necessary. A small, thin-walled, iron cylinder, *G* (Fig. 4), was used, in which the nitrate was heated. It is fitted with a cover containing a glass observation tube, *D*, plugged with glass wool, and a hole just large enough to take the tube *F*. The other part of the apparatus consists of two flasks, *A* and *B*, thoroughly dried and connected by means of capillary tubing with a three-way tap, all joints being sealed with paraffin wax. The apparatus having been tested for the maintenance of a vacuum, the flasks are exhausted in turn by means of a Fleuss pump.

A charge of nitrate is inserted and the temperature gradually raised: white fumes, which consist of sublimed ammonium nitrate, appear in the observation tube, *D*; during this interval, nitrous oxide is evolved as usual and drives out the air from the apparatus. Further heating causes red fumes to appear, and almost immediately there follows an explosion which blows out the plug *E*. The end of *F* is now inserted well into the cylinder so that the

end reaches under the tube *D*. By turning the tap *C*, first one and then the other flask is filled with the gas from *G*, the nitrous oxide having been driven out when the explosion occurred. The object of the tube *D* is to provide a means of ascertaining that there is no back-rush of gas when the flasks are being filled. Thus there are two samples of gas ready for analysis. From preliminary experiments, it was found that the gases contained large quantities of nitric oxide and nitrogen peroxide, whilst the amount of nitrous oxide seemed to be very small. Hence a new method of analysing the gases was employed. The end of the tube *F* is inserted in a known volume of standard permanganate solution acidified with

FIG 4.

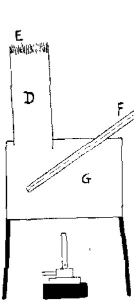
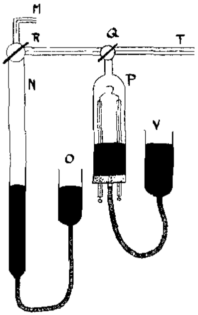


FIG. 5.



sulphuric acid, and the tap opened, when a little of the solution enters the flask. The solution is decolorised, a partial vacuum produced, and the tap is again opened; this process is repeated, the permanganate being each time allowed to enter and well shaken, until the solution is no longer decolorised, the unchanged permanganate showing that the absorption of nitric oxide is complete. The residual gas is now measured at atmospheric pressure. The end of the tube *F* is connected with a suitable gas burette, *N* (Fig. 5), and the reservoir, *O*, is lowered so that the air in the capillaries is drawn into *N* and then expelled through *S* and *T*. The flask, *B*, is put in communication with *N*, and the reservoir, *R*, lowered until the mercury stands at the zero mark. The tap, *R*, is closed, the levels of the mercury are adjusted, and the true

volume is found. Knowing the volume of the flask and the volume of the liquid it contains, the true volume of the gas may be calculated. This sample of gas is then used for the estimation of nitrous oxide. There will be a slight error due to the solubility of this gas in the permanganate, but it will never exceed 1 per cent. under the conditions of these experiments, and a correction may be applied. The nitrous oxide is estimated as described on p. 700. The method of estimating nitric oxide and nitrogen peroxide is carried out as follows. The remainder of the permanganate is admitted to the flask, the tap opened, and the cork removed. The whole of the permanganate is then titrated with $N/2$-ferrous sulphate until it is colourless. It is best to use a slight excess to dissolve any precipitate that may be formed, and to determine the end-point by back-titration. The volume of permanganate reduced by the sample of gas is thus determined. The total combined nitrogen is found by the method of Bowman and Scott. A known volume of the above solution (permanganate and ferrous sulphate) is run with careful cooling into ten times its volume of concentrated sulphuric acid, and then titrated with ferrous sulphate until a brownish-pink colour appears. At this stage the whole of the nitrates produced by the oxidation with permanganate has been reduced to nitrous acid. The colour change requires 0·2 c.c., which is subtracted from the volume observed. In these experiments, there is yet another source of error—the presence of nitric acid vapour and ammonium nitrate among the gaseous products of decomposition. To determine what correction has to be made, the second bulb, A, filled with the same sample of gas, is utilised. By means of the three-way tap a little dilute sodium hydroxide solution is allowed to enter the bulb; this dissolves any nitrate, and combines with the nitrogen peroxide and nitric acid. In order that the nitric oxide shall not interfere with the result (owing to oxidation and then combination with the alkali), it is removed by means of the pump, and air admitted. Then another estimation is carried out as before.

By the permanganate titration, the amount of nitrogen peroxide is calculated. Then, by the ferrous sulphate titration, the total nitrate is found. If this is in excess of that demanded by the amount of nitrogen peroxide present, the corresponding correction to be used in the analysis of the contents of B is applied. If a = c.c. of $N/2$-permanganate reduced by the gas in the first titration, and b = c.c. of $N/2$-ferrous sulphate required in the second titration, after subtracting the above correction, then the volumes of nitrogen peroxide and of nitric oxide at $N.T.P.$ are $2{\cdot}8\,(3b - 2a)$ c.c. and $2{\cdot}8\,(2a - b)$ c.c. respectively.

TABLE VI.

Explosive decomposition.

In each case the amounts of nitric oxide and nitrogen peroxide are calculated from the formula, and the remaining gases calculated to *N.T.P.* and percentages taken.

No. of expt. :—	1	2	3	4	5
C.c. of $N/2$-$KMnO_4$	16·28	15·7	8·9	16·0	15·7
C.c. of $N/2$-$FeSO_4$	14·3	13·3	7·5	14·6	14·6
Vol. of NO_2	29	23·7	12·9	33	34·7
Vol. of NO	51·2	50·3	28·9	48·7	52
Vol. of remaining gases	76	76	42	80	82
N_2O in ,, ,, ...	— †	6 *	8 *	17	— †
NO_2 per cent.	18·6	15·8	15·4	20·4	20·6
NO ,, ,, ...	32·7	32·7	34·5	30·2	30·8
N_2O ,, ,, ...	—	3·1	4	8·4	—
N_2 ,, ,, (by diff.)	48·7	47·5	46·1	41·0	48·5

* These mixtures refused to explode, so sparks were passed until there was no further contraction.

† The quantity of nitrous oxide is less than 5 per cent. and impossible to estimate under the conditions of the experiment; it is therefore included with the nitrogen.

As may be seen from these results, the decomposition at the lowest temperature at which an explosion will occur is very different from that which occurs normally. The amount of nitrous oxide is greatly diminished, and the gas contains nitrogen peroxide, nitric oxide, and nitrogen in the approximate ratio 2 : 4 : 5.

	Percentage composition of the gas, neglecting N_2O.	Percentage composition calculated for the ratio 2 : 4 : 5.
Nitrogen peroxide	18·4	18·2
Nitric oxide	32·7	36·3
Nitrogen	46·3	45·5

The agreement is sufficiently close, considering the nature of the experiments, to justify the statement that the main course of the reaction is :

$$8NH_4NO_3 \longrightarrow 16H_2O + 2NO_2 + 4NO + 5N_2.$$

The explosion is accompanied by a yellow flame not unlike that of ammonia burning in oxygen.

Summary of Results.

Pure ammonium nitrate decomposes into nitrous oxide and water to the extent of 98 per cent., the course of the decomposition remaining unaltered over a range of temperature from 210° to 260°.

At some point near 300° other oxides of nitrogen are evolved, the action proceeding explosively.

Nitrogen is always present; with the pure nitrate up to 260°, 2 per cent.; immediately after explosion, 46 per cent.; in the case of chloride mixtures, 30—50 per cent.

At the moment of explosion, the nitrate decomposes in a totally different manner, giving nitrogen peroxide, nitric oxide, and nitrogen in the ratio 2 : 4 : 5.

With the pure nitrate, the rate of evolution of the gas is dependent on the temperature and on the mass of material; but *when any impurity is present, this does not necessarily hold good.*

With chlorides, a quantity as small as 0·1 per cent. has a very marked influence on the decomposition, chlorine being invariably present in the gas evolved.

The quantity of chlorine is proportional to the amount of chloride and to the temperature.

When chlorides are present, the rate of evolution of gas is very much accelerated, the addition of 1 per cent. producing a result comparable with that caused by a rise of temperature of 25—30° in the case of the pure nitrate.

The higher the initial temperature, the poorer the gas is in nitrous oxide for any given mixture.

At any given temperature the amount of chlorine falls off as time goes on, and the composition of the gas approximates to that given by the pure nitrate at the same temperature.

The liquid products of the reaction in these cases always contain hydrochloric acid as well as nitric acid.

Sulphates are without characteristic action.

Sodium nitrate in small quantities does not influence the decomposition at temperatures below 250°.

This work was undertaken at the suggestion of Dr. E. P. Perman. I desire to express my indebtedness to him for his helpful criticism.

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[*Received, November 26th, 1921.*]

LXXXII.—*Note on the Effect of Electrolytes on the Constitution of Soap Solutions, as Deduced from Electromotive Force.*

By CYRIL SEBASTIAN SALMON.

THE experiments here recorded were carried out to determine the equilibria in soap solutions containing potassium and sodium chlorides in concentrations insufficient for salting out. The method

adopted was to measure by means of the *E.M.F.* the concentration (activity) of both ions of the added electrolytes and thus obtain the proportion of soap present as ionic micelle ; this being given by the excess of alkali over the chlorine ion. The effect of sodium chloride on sodium palmitate was investigated at 90°, and of potassium laurate at room temperature.

The alkali metal ions were studied by means of the corresponding amalgam electrode as described for pure soap solutions (Salmon, T., 1920, **117**, 530), and the chlorine ion by means of silver chloride electrodes. Attempts were first made to determine the concentration of the latter ion by means of the chlorine gas electrode, but they were discontinued on account of the effect of the chlorine on the soap.

The silver chloride electrodes were prepared as follows: A small piece of silver gauze was fused to a piece of silver wire and the latter sealed into a glass tube. The gauze was then covered with silver electrolytically, and was finally made the anode in a dilute solution of potassium chloride. The deposit of silver chloride obtained in this manner was dark in colour, as described by MacInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445). These electrodes were prepared in pairs, which, after being tested for equality, were used as opposite electrodes in concentration cells with potassium chloride.

In this case, where the greater part of the current is carried by potassium chloride, the liquid potentials are small, but they were investigated. Table I contains the results of the measurements, and in the last coloumn is given the *E.M.F.* of the cells in which a correction has been introduced for diffusion potential. No correction could be made in the case of sodium palmitate, because the *E.M.F.* observed was independent of the concentration of the sodium chloride to within one millivolt over the range 0·2 to 0·01*N*. The temperature gradient between 90° and 18° in the case of sodium palmitate was always kept within the middle solution of sodium chloride.

The concentrations of the ions calculated from these data are shown in Table II. The alkali metal ions are calculated by comparison with 0·2*N*-potassium chloride at 18° for potassium soaps and 0·2*N*-sodium chloride at 90° for sodium soaps, assuming, from conductivity data, dissociations of 83·5 and 80·5 per cent. respectively. The chlorine ions are calculated directly from the *E.M.F.* of the concentration cells, and in the case of sodium palmitate are corrected for the expansion produced on heating the sodium palmitate solutions to 90°. All ionic concentrations are expressed in volume normalities.

TABLE I.

$K_xHg|aN$-KL, bN-KCl|cN-KCl|0·1N-KCl, Hg_2Cl_2 (solid)|Hg.

a.	b.	c.	Volts. Obs.	Corr.
0·00	0·2	0·2	−2·106	−2·106
1·0	1·0	,,	−2·068	−2·067
,,	,,	0·05	−2·068	−2·067
,,	,,	0·01	−2·069	−2·067
,,	0·5	0·2	−2·086	−2·085
,,	,,	0·05	−2·087	−2·085
,,	,,	0·01	−2·089	−2·085
0·5	1·0	0·2	−2·069	−2·069
,,	,,	0·05	−2·070	−2·069
,,	,,	0·01	−2·070	−2·069
,,	0·5	0·2	−2·085	−2·085
,,	,,	0·05	−2·087	−2·085
,,	,,	0·01	−2·088	−2·085

Ag|AgCl (solid), aN-KL, bN-KCl|0·05N-KCl, AgCl (solid)|Ag.

a.	b.	Obs.	Corr.
1·0	1·0	−0·069	−0·068
,,	0·5	−0·051	−0·049
0·5	1·0	−0·068	−0·067
,,	0·5	−0·049	−0·047

$Na_xHg|dN$-NaP(90°), eN-NaCl|0·2N-NaCl|0·1N-KCl(18°)|0·1N-KCl, Hg_2Cl_2(solid)|Hg.

d.	e.	Obs.	Corr.
0·00	0·2	−2·241	−2·241
1·0	0·4	−2·222	−2·222
0·4	0·4	−2·225	−2·225

Ag|AgCl(solid),dN-NaP(90°),0·4N-NaCl|0·1N-KCl(18°)|0·05N-KCl,AgCl (solid)|Ag.

d.	Obs.	Corr.
1·0	−0·059	−0·059
0·4	−0·056	−0·056

TABLE II.

Concentrations of chlorine and potassium or sodium ions, and hence, by difference, of the ionic micelle.

Solution.		Cl′.	K˙ or Na˙.	Ionic micelle.
1·0 N-KL	+1·0 N-KCl	0·70 N	0·79 N	0·09 N
1·0 ,,	+0·5 ,,	0·32 ,,	0·38 ,,	0·06 ,,
0·5 ,,	+1·0 ,,	0·67 ,,	0·73 ,,	0·06 ,,
0·5 ,,	+0·5 ,,	0·30 ,,	0·38 ,,	0·08 ,,
1·0 N-NaP	+0·4 N-NaCl	0·29 ,,	0·33 ,,	0·04 ,,
0·4 ,,	+0·4 ,,	0·28 ,,	0·30 ,,	0·02 ,,

Discussion.

Although, from the nature of the measurements, no stress can be laid on the accuracy of the final results, they serve to show the great effect which addition of electrolyte has in driving back the

dissociation of the colloidal electrolyte. This is shown very clearly in Table III, where comparison is made between the concentration of ionic micelle in the soap solution before and after the addition of the inorganic salt. In the case of potassium laurate there is present practically no crystalloid other than potassium ion even in the absence of potassium chloride, so that the concentration of neutral colloid can also be directly calculated. Similarly, with N-sodium palmitate, all the soap must be in colloidal form, as ionic micelle and as neutral colloid. On the other hand, there is too much of the $0{\cdot}4N$-sodium palmitate present as crystalloidal palmitate ion and sodium palmitate to permit of the evaluation of the neutral colloid without using other data.

TABLE III.

Concentrations of ionic micelle and of neutral colloid in soap solutions with and without addition of a salt.

		Soap only.	Mixture.	Soap only.	Mixture.
1·0 N-KL	+1·0 N-KCl	0·35	0·11	0·62	0·89
1·0 ,,	+0·5 ,,	0·35	0·07	0·62	0·93
0·5 ,,	+1·0 ,,	0·18	0·07	0·31	0·43
0·5 ,,	+0·5 ,,	0·18	0·09	0·31	0·41
1·0 N-NaP	+0·4 N-NaCl	0·28	0·05	0·50	0·95
0·4 ,,	+0·4 ,,	0·09	0·02	0·08	0·38

A glance at Table III *shows the great effect of the inorganic salt* in diminishing the amount of ionic micelle, leaving the soap largely in the form of neutral colloid. The data do not permit of closer comparison of the different solutions with each other.

Some theoretical interest attaches to the comparison of the values obtained for the concentrations of chlorine ion in these soap mixtures with those which have been determined by other observers for the same salt solutions in the absence of soap. The activity of the chlorine ion in $0{\cdot}5N$-potassium chloride is 0·31 as compared with 0·30 after addition of $1{\cdot}0N$-potassium laurate. The available data show that the apparent concentration of chlorine ion, as measured by the *E.M.F.*, is not affected by the presence of these large amounts of soap within the experimental error. We know that about one-fifth of the solvent water is removed by hydration of the soap, but this effect is compensated by the corresponding increase in the volume of solution when the soap is added.

Conclusion.

Soap solutions containing an electrolyte with a common ion are found to be largely in the form of undissociated neutral colloid, the amount of ionic micelle being very much smaller than in the pure soap solutions.

The activity of the chlorine ion in potassium chloride solutions appears to be unaffected by the addition of quite large quantities of potassium laurate owing to the compensating effect of the great enhancement of bulk caused by the addition of the soap and the removal of an appreciable fraction of the solvent through hydration of the soap.

My thanks are due for grants from the Colston Research Society of the University of Bristol and from the Research Fund of the Chemical Society. My thanks are also due to Professor J. W. McBain for his constant interest and advice.

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THE UNIVERSITY, BRISTOL. [*Received, March 11th, 1922.*]

LXXXIII.—*Preparation of* p-*Nitrophenylhydrazine and other Aromatic Hydrazines.*

By WILLIAM DAVIES.

THE preparation of *p*-nitrophenylhydrazine by an entirely satisfactory method has not hitherto been described. The reduction of *p*-nitrobenzenediazonium chloride by potassium sulphite (Bamberger and Kraus, *Ber.*, 1896, **29**, 1834) results in a good yield, but the cost and sometimes inaccessibility of potassium salts are a drawback to this method. Bischler and Brodski (*Ber.*, 1889, **22**, 2815) attempted the reduction of *p*-nitrobenzenediazonium chloride by stannous chloride in the usual way, but merely obtained tarry material and a small quantity of *p*-phenylenediamine. Several experiments under various conditions have practically confirmed this result, for a yield of about 1 per cent. of *p*-nitrophenylhydrazine was the highest obtained.

p-Nitrophenylhydrazine has already been prepared (Bamberger and Kraus, *loc. cit.*) by Fischer's method (*Annalen*, 1878, **190**, 77). Purgotti (*Ber.*, 1892, **25**, 119) obtained *p*-nitrophenylhydrazine and a resinous by-product by the action of sodium hydrogen sulphite solution on *p*-nitrobenzenediazonium chloride, and a patent (D.R.-P. 62004) is based on this method. A repetition of Purgotti's preparation and of the process described in the patent resulted in a small yield of the hydrazine and a large amount of resinous substance.

An investigation of the reduction of 1 gram-molecule of *p*-nitrobenzenediazonium chloride by excess of sodium sulphite solution shows that approximately 1 gram-molecule of sodium hydroxide is produced in the reaction. The course of the reaction (i) between

benzenediazonium chloride and sodium sulphite (E. Fischer, *loc. cit.*, p. 79) is therefore quite distinct from that (ii) taking place between *p*-nitrobenzenediazonium chloride and sodium sulphite.

(i) $PhN_2Cl + 2Na_2SO_3 + H_2O = PhN_2H_2{\cdot}SO_3Na + NaCl + Na_2SO_4$.

(ii) $NO_2{\cdot}C_6H_4{\cdot}N_2Cl + 2Na_2SO_3 + H_2O = NO_2{\cdot}C_6H_4{\cdot}N_2H(SO_3Na)_2 + NaCl + NaOH$.

(iii) $RN_2Cl + Na_2SO_3 = RN_2{\cdot}SO_3Na + NaCl$.

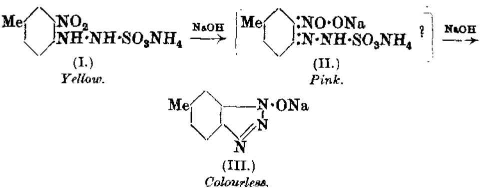
The initial reaction with 1 molecule of sulphite doubtless takes the same direction (iii) in each case, but it is remarkable that the presence of the para-standing nitro-group should make the disulphonate formed comparatively stable. This *p*-nitrophenylhydrazine-*disulphonate is extremely soluble in water and has not been isolated*, as it easily suffers partial hydrolysis to the monosulphonate.

An important factor in the success of the preparation is maintaining the sulphite solution neutral or alkaline throughout the addition of the diazo-solution. Otherwise (or when sodium hydrogen sulphite is used) the diazo-sulphonate separates out as an unstable, orange mass, which redissolves to react with more sodium sulphite with difficulty, but readily decomposes with the formation of a resin. This circumstance sufficiently explains the production of the large amount of resin by Purgotti's method. The detailed preparation by means of which a yield of 80 per cent. of the pure hydrazine can be obtained, without any resinous by-product, is described in the experimental portion of this communication.

The replacement of sodium sulphite in the preparation of *p*-nitrophenylhydrazine by ammonium sulphite is, owing to the sparing solubility of ammonium *p*-nitrophenylhydrazinedisulphonate, very advantageous.

The great solubility of ammonium sulphite as compared with that of sodium sulphite gives the former substance a great advantage in the preparation of aromatic hydrazines. Not only is the bulk of liquid kept down, but also the intermediately formed ammonium hydrazinesulphonates are often (although not invariably) only slightly soluble in water. For example, the addition of benzene-*diazonium chloride to a concentrated solution of ammonium* sulphite causes the separation of a large quantity of ammonium phenylhydrazinesulphonates, which on hydrolysis produce phenylhydrazine hydrochloride in a yield of about 60 per cent. of the theoretical. The total yield is about 80 per cent.

The preparation of *m*-nitro-*p*-tolylhydrazine furnishes a very interesting instance of the great ease with which benzotriazoles are formed.



The preparation of benzotriazoles from hydrazines by the action of alkalis on stable neutral salts like the sulphonates has apparently hitherto not been observed. The remarkable ease with which the hydrolysis of the ammonium sulphonate takes place with alkali is probably a measure of the great tendency shown by *o*-nitrophenylhydrazines to pass into the corresponding benzotriazoles.

In conclusion, it may be mentioned that aqueous solutions of *p*-nitrophenylhydrazine hydrochloride and of *m*-nitro-*p*-tolylhydrazine hydrochloride are extremely useful reagents for the detection of aldehydes or ketones which are at all miscible with water. The reaction

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2,HCl + R_1R_2CO = NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CR_1R_2 + H_2O + HCl$$

in dilute solution rapidly goes almost to completion owing to the ease with which the hydrochloride is hydrolysed and to the insolubility of the hydrazone in water. Moreover, acetals and certain derivatives of aminoacetal are transformed under similar conditions to the hydrazones of the corresponding aldehyde. In these respects the nitrohydrazines described have an advantage over phenylhydrazine itself.

EXPERIMENTAL.

Preparation of p-*Nitrophenylhydrazine by means of Sodium Sulphite.*—A solution of *p*-nitrophenyldiazonium chloride prepared from 10 grams of *p*-nitroaniline and 21 c.c. of hydrochloric acid (36 per cent.) is filtered and slowly added with continuous stirring to an ice-cold solution of 41 grams of sodium sulphite (90 per cent. $Na_2SO_3,7H_2O$) in 100 c.c. of water containing 4 grams of sodium hydroxide. The addition requires about five minutes; if the diazonium solution is added too rapidly, an orange-red precipitate of sodium *p*-nitrodiazobenzenesulphonate is produced, and is apt to form a resin. Having remained for five minutes, the solution is acidified with concentrated hydrochloric acid (70 c.c.) and heated on the water-bath at 55° for three minutes, when yellow needles

begin to separate. On the next day the crystals are heated with concentrated hydrochloric acid (20 c.c.) on the water-bath for seven minutes, and after cooling and keeping, the precipitate of sodium salts and of *p*-nitrophenylhydrazine hydrochloride is dissolved in water and treated with a cold concentrated solution of sodium acetate, when the free base (7—8 grams) at once separates. It is practically pure and crystallises from alcohol in light brown leaves melting with decomposition at 157°. The yield is increased to 9 grams by carefully neutralising the acid filtrate from the crude *p*-nitrophenylhydrazine hydrochloride with ice-cold sodium hydroxide solution, and hydrolysing as before with sodium acetate solution.

If a larger quantity of hydrochloric acid is used in the diazotisation of the *p*-nitroaniline, an equivalent quantity of alkali must be added to the sulphite solution. When the preparation is carried out on a much larger scale, it may not be necessary to maintain the temperature at 55° for three minutes owing to considerable hydrolysis taking place between room temperature and 55° during the comparatively slow heating and cooling. This precaution is mentioned, as the hydrolysis to the hydrazine hydrochloride is undesirable at this stage.

Sodium *p*-nitrophenylhydrazinemonosulphonate consists of minute, lemon-yellow needles decomposing when slowly heated at about 107° (Found: S = 10·9. Purgotti's formula, $C_6H_6O_5N_3SNa,2H_2O$, requires S = 11·0 per cent.). The solubility at 12° is about 2·4, but is much greater in hot water. The salt dissolves in cold sodium hydroxide solution and in concentrated ammonia with the production of a clear red solution which becomes yellow again on acidification. The monosulphonate reduces Fehling's solution readily at 35°.

Some sodium *p*-nitrophenylhydrazinemonosulphonate separates when the reaction product from the sulphite and diazonium solutions is treated with excess of concentrated hydrochloric acid and the solution left over-night. The following considerations show that the hydrochloric acid has no mere salting-out effect, but must cause partial hydrolysis of the disulphonate even in the cold.

Proof of the Initial Formation of the Disulphonate.—The extremely slow addition of a faintly acid solution of *p*-nitrophenyldiazonium chloride to perfectly neutral sodium sulphite solution resulted in the production of a strongly alkaline liquid. The estimation of the sodium hydroxide produced in the reaction was carried out as follows: Finely powdered *p*-nitroaniline (10·00 grams) was covered with concentrated hydrochloric acid (21·00 c.c.; *d* 1·186) and diazotised with a solution of sodium nitrite (5·55 grams

of 90 per cent. $NaNO_2$) in 10 c.c. of water. The filtered diazonium solution was added slowly and with continual stirring to the sulphite solution, which had been prepared by dissolving sodium sulphite (42 grams of 91 per cent. $Na_2SO_3,7H_2O$) in 150 c.c. of water, neutralising with hydrochloric acid (phenolphthalein indicator), and then adding 50 c.c. of sodium hydroxide solution containing 38·46 grams of NaOH per litre. The red reaction liquid, after standing for half an hour, was titrated with *N*-hydrochloric acid, of which 17·5 c.c. were required, phenolphthalein being the indicator. The end-point was found quite definitely by making clearly acid, diluting the yellow solution produced, and titrating back with standard alkali. Assuming that the impurity in the sodium nitrite was sodium nitrate and that this substance had no effect on the course of the reaction, 2·917 grams of sodium hydroxide had been produced in the reaction. One gram-molecule of *p*-nitroaniline would therefore, when subjected to the above reactions, produce 40·25 grams (or very nearly 1 gram-molecule) of sodium hydroxide. When it is also considered that the alkaline reaction product does not reduce Fehling's solution, and does not deposit crystals on neutralisation, as would be expected if the slightly soluble, easily oxidisable monosulphonate were present, it is evident that the course of the reaction between *p*-nitrobenzenediazonium chloride and sodium sulphite is quantitatively expressed by equation (ii) and not by equation (i).

Preparation of p-*Nitrophenylhydrazine by means of Ammonium Sulphite.*—A saturated solution of ammonium sulphite is readily prepared by passing sulphur dioxide into a mixture of one part of ammonia solution (*d* 0·880) and two parts of powdered ice in a freezing mixture. The liquid smells finally of sulphur dioxide and is then neutralised with ammonia. Such a solution at room temperature deposits ammonium sulphite crystals and contains about 0·25 gram of sulphur dioxide per c.c.

p-Nitroaniline (10 grams) is diazotised as already described and the filtered solution slowly added with stirring to a cold saturated solution of ammonium sulphite (40 c.c.) containing 8 c.c. of concentrated ammonia solution. Efficient cooling is necessary, for ammonium *p*-nitrophenylhydrazinedisulphonate quickly separates with the evolution of much heat. The product is filtered after remaining for an hour in the freezing mixture, and the yellow precipitate heated on the water-bath with concentrated hydrochloric acid (20 c.c.) for seven minutes at 70—80°. The blood-red solution is cooled, the precipitate of *p*-nitrophenylhydrazine hydrochloride and ammonium salts dissolved in water, and the pure free base isolated as already described, when a yield of 9 grams of *p*-nitrophenylhydrazine is obtained.

Ammonium p-*nitrophenylhydrazinedisulphonate* consists of minute, yellow needles which, when slowly heated, decompose at 105—109° (* Found: S = 17·5. $C_6H_{13}O_8N_5S_2,H_2O$ requires S = 17·5 per cent.). Its solubility at 12° is about 4·5, and is much greater at 100° and smaller at 0°. It does not reduce Fehling's solution. An aqueous suspension of the salt dissolves readily in sodium hydroxide solution with a deep red coloration [doubtless forming the trisodium disulphonate, $NO_2{\cdot}C_6H_4{\cdot}N(SO_3Na){\cdot}NNa{\cdot}SO_3Na$], but concentrated ammonia solution has a very slight solvent action, the yellow solution merely becoming somewhat more deeply yellow.

m-*Nitro*-p-*tolylhydrazine*.—This substance is prepared by adding *m*-nitro-*p*-toluenediazonium chloride to concentrated ammoniacal ammonium sulphite, keeping for half an hour, and partly hydrolysing the soluble disulphonate with hydrochloric acid on the water-bath at 55° (exactly as described in the preparation of *p*-nitrophenylhydrazine) until the sparingly soluble, yellow ammonium hydrazinemonosulphonate begins to separate from the warm solution. The sulphonate is collected and heated with concentrated hydrochloric acid at 80°, when the hydrochloride of the hydrazine is formed. The free base, isolated in the same way as *p*-nitrophenylhydrazine, crystallises from alcohol in scarlet needles melting at 110° (compare Pope and Herd, T., 1901, **79**, 1142).

Ammonium m-*nitro*-p-*tolylhydrazinesulphonate* (I) is readily soluble in hot and sparingly soluble in cold water, from which it crystallises in deep yellow needles (Found: in air-dried material, S = 11·7. $C_7H_{12}O_5N_4S$ requires S = 12·1 per cent.). The interest attaching to this substance lies in its behaviour towards cold alkali. The yellow, aqueous solution of the sulphonate instantly becomes pink on the addition of sodium hydroxide solution and then rapidly colourless. By titration with *N*/10-sodium hydroxide it is found that 1 gram-molecule of the ammonium sulphonate requires 83 grams (or approximately 2 gram-molecules) of sodium hydroxide to complete the reaction and to form a neutral solution. Excess of sodium carbonate solution has the same effect as the caustic alkali, but the existence of the pink coloration is more prolonged. A large excess of ammonia will also ultimately produce a colourless solution, but sodium acetate apparently will not. The change of colour is most strikingly observed by pouring sodium hydroxide solution on the solid sulphonate, which instantly becomes red and rapidly dissolves to a colourless solution. Such a solution, when acidified,

* Air-dried at 30°. The sulphonate was hydrolysed by boiling with concentrated hydrochloric acid for ten minutes, and the sulphuric acid produced estimated in the usual way.

slowly deposits colourless, feathery needles melting with decomposition at 176° (uncorr.), and agreeing in other properties with 1-hydroxy-6-methyl-1 : 2 : 3-benzotriazole (III) (Zincke and Schwarz, *Annalen*, 1900, **311**, 340).

Summary.

The course of the reaction between *p*-nitrobenzenediazonium chloride and sodium sulphite has been elucidated, and an inexpensive and extremely convenient substance for the preparation of *p*-nitrophenylhydrazine and other phenylhydrazines has been discovered in ammonium sulphite.

The thanks of the author are due to Professor Lapworth, F.R.S., for the interest he showed in the work, which was carried out in 1917—1918.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY, MANCHESTER. [*Received, February* 16*th*, 1922.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 30TH, 1922, AT 4.30 P.M.

SIR JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

THE TREASURER made a statement as to the present financial position of the Society. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending 31st December, 1921, was then proposed by PROFESSOR P. P. BEDSON, seconded by DR. F. L. PYMAN, and carried unanimously.

REPORT OF COUNCIL, 1921-1922.

IT is satisfactory to report that notwithstanding the increase in the amount of the Annual Subscription from £2 to £3 beginning with the year under review, the number of Fellows elected during 1921 exceeded that of any previous year, and that the membership continues steadily to increase.

On December 31st, 1920, the number of Fellows was 3,721. During 1921, 349 Fellows were elected and 7 reinstated, making a gross total of 4,077. The Council regrets that the number of deaths has been unusually heavy, no fewer than 51 Fellows having died; 49 resignations have been accepted, as against 92 the previous year; the names of 54 Fellows have been removed for non-payment of Annual Subscriptions, whilst the election has been declared void in the cases of 11 newly elected Fellows who neglected to pay the necessary fees. On the 31st December, 1921, the Society numbered 3,912 Fellows, showing an increase of 191 over that of the previous year.

The congratulations of the Society are offered to the following, who have attained their jubilee as Fellows:

	Elected.
William Howarth Darling	May 4th, 1871.
Mortyn John Salter	June 15th, 1871.
Henry Richardson Procter	June 15th, 1871.
George Joseph Warner	Dec. 7th, 1871.
William John Wilson	Dec. 7th, 1871.
John Millar Thomson	Jan. 18th, 1872.
Robert Barton	Jan. 18th, 1872.
William Thomson	Jan. 18th, 1872.
Charles Frederick Chandler	Jan. 18th, 1872.
John Watts	Feb. 1st, 1872.
Robert William Atkinson	Mar. 7th, 1872.

It was with the deepest regret that the Council received the news of the death of Dr. H. R. Le Sueur, which took place on the 9th July. Dr. Le Sueur held the office of Secretary from March 1920, and the Council has placed on record its appreciation of his services to the Society and its sense of the loss which chemical science in general and the Society in particular suffered by his death.

The Council appointed Dr. Irvine Masson as Secretary until the next Annual General Meeting, to fill the vacancy caused by Dr Le Sueur's lamented death.

The Council has to mourn the loss of one of its distinguished Honorary Fellows, Professor Giacomo Ciamician, who was elected on March 2nd, 1911.

The volume of Transactions for 1921 contains 2,135 pages, of which 1,990 pages are occupied by 243 memoirs, the remaining 145 pages being devoted to Obituary Notices, lectures on special subjects, the Report of the Annual General Meeting, the Presidential Address, and the Report of the International Committee on Physico-chemical Symbols. The volume of the preceding year contained 182 memoirs, occupying 1,486 pages. The Journal for 1921 contains also 4,005 abstracts, occupying 1,636 pages, whilst the abstracts for 1920 numbered 4,074, and occupied 1,708 pages. The decrease in the number of abstracts appearing in 1921 was caused by the very great delay in transmission of some of the foreign journals during the latter portion of the year. In consequence of this a considerable number of abstracts which should have appeared in the 1921 volume will be found in the Journal for 1922.

The abstracts may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	—	1474
Physiological Chemistry	—	317
Chemistry of Vegetable Physiology and Agriculture ...	—	232
	916	2023
PART II.		
General and Physical Chemistry	—	1003
Inorganic Chemistry	—	331
Mineralogical Chemistry	—	61
Analytical Chemistry	—	587
	720	1982
Totals in Parts I and II.	1636	4005

To meet the convenience of Fellows, arrangements were made to exchange a limited number of sets of the Journal of the Chemical

Society from August 1914 to the end of 1920 for an equal number of sets of the publications of the German Chemical Society.

The Council has pleasure in directing the attention of Fellows to the bust of the late Mr. John J. Griffin, an Original Member of the Society, which has been presented by Miss Griffin and placed in the Council Room. Thanks are due also to Mrs. Blount for a gift of two special balances used by the late Mr. Bertram Blount.

Owing to the continued increase in the number of papers communicated to the Society, the Council arranged for the current session to commence in October instead of November, and to hold the special lectures on days other than those devoted to Ordinary Scientific Meetings. These lectures on special subjects appear to meet with the keen appreciation of Fellows. On December 8th, Professor J. W. Gregory lectured on "The Genesis of Ores," Sir Ernest Rutherford's lecture entitled "Artificial Disintegration of Elements" was delivered on February 9th, and there remains to be given on June 8th, 1922, Dr. H. H. Dale's lecture on "Chemical and Physiological Properties."

The Council has invited Prof. W. H. Perkin to deliver the von Baeyer Memorial Lecture during the present year.

The thanks of the Council are tendered to the Contributors to the Annual Reports for 1921 and to the Abstractors for their services during the past year.

The Gerhardt Memorial at Strasbourg, towards which Fellows had subscribed a sum of more than £200, was unveiled on July 5th, 1921.

Arrangements were again made by which Members of the American Chemical Society could obtain the current Annual Reports at 7*s*. per copy post free, and more than 200 applications were received. A like privilege has been accorded to Members of the Society of Chemical Industry in response to that Society's offer of Vol. VI of the Annual Reports on the Progress of Applied Chemistry to Fellows of the Chemical Society at the reduced price of 10*s*. per copy.

Reference was made in the last Report of Council to the Conference held in July, 1920, to consider whether economies could be effected in the construction and equipment of chemical laboratories. The Committee appointed to carry out the recommendations of the Conference collected details of practice and experience in a large number of laboratories, regarding materials used and methods of construction. The Report embodying the results of these inquiries received the approval of the Conference and was ordered by the Council to be printed in pamphlet form and issued to applicants free of charge. Copies of this Report

can be obtained from the Assistant Secretary. The expenses incurred in connexion with the inquiry have been defrayed by a grant from the Research Fund.

The Report and List of Physico-chemical Symbols, to which reference was made last year, were printed in the Journal for April and issued in pamphlet form to applicants free of charge.

The Committee which, as recorded in the last Report of Council, was appointed to deal with the question of the testing of graduated glassware, met, at the instance of the National Physical Laboratory, to consider the further question of setting up a recognised standard of accuracy for "commercial grade" volumetric glassware. The question was further considered at a Conference summoned by the National Physical Laboratory and was ultimately referred to a Standing Committee on which Professor A. J. Allmand and Dr. Bernard Dyer act as the Society's representatives.

As intimated in the circular letter issued on January 27th, 1922, to Fellows resident in the British Isles, arrangements have been made by which Fellows of the Chemical Society are to be afforded the opportunity of reading papers on pure chemistry at meetings of the Provincial Local Sections of the Society of Chemical Industry. All papers thus read will, if the author so desires, be forwarded to the Chemical Society and will be considered for publication in the Transactions as if they had been communicated direct to the Chemical Society. The experiment will be made in the following centres: Birmingham, Bristol and S. Wales, Edinburgh, Glasgow, Liverpool, Manchester, Newcastle, Nottingham, and Yorkshire (Leeds), and it is hoped that this scheme will be in full operation by next session at the latest, and that every advantage will be taken of the privilege by Fellows residing near these centres.

The President was appointed to represent the Society on the General Committee of the British Empire Exhibition to be held in 1924. Permission was given for the Chemical Society to be included amongst the list of Patrons of the Coal Smoke Abatement Society Exhibition, and Professor J. B. Cohen and Mr. E. V. Evans were nominated to represent the Society on the Exhibition Council.

Sir Robert Robertson and Professor S. Smiles were appointed to represent the Society on the Conjoint Board of Scientific Societies for 1922, and Professor H. E. Armstrong, Professor J. C. Philip, and Sir William Pope were nominated as the Society's representatives on the Federal Council.

In September last the President issued to Fellows an Appeal on behalf of Russian scientific men for donations, gifts of clothing, and recent chemical literature. The Council is glad to state that up to the present the sum of £207 17*s*. 10*d*. has been received in

response to this appeal, in addition to parcels of clothing and books which have been dispatched to Petrograd and Moscow.

The extension of the Library on the technical side and the increased hours of opening continue to be appreciated by those using the Library, as is shown by the fact that the total attendances for 1921 more than double the figures for the year previous to this development. During the additional hours in which the Library is now open, 1,609 attendances were recorded in 1921, as against 1,550 in 1920.

During 1921 the total cost of the Library approximated to £1,800 (including £240 for additional shelving), and towards this the contributing Societies subscribed £416 5*s*. The Council trusts that these Societies will continue to support the Library in as generous a measure as possible.

The additional shelving provided by the completion of the second basement store will afford accommodation until 1926 at the present rate of growth, after which further accommodation will be needed.

The books borrowed from the Library during 1921 numbered 3,585, as compared with 3,079 in 1920. The additions to the Library comprise 244 books, 441 volumes of periodicals, and 168 pamphlets, as against 312 books, 439 volumes of periodicals, and 196 pamphlets last year.

It will be remembered that the accounts for the year 1920 revealed an apparent deficit of £1,310 6*s*. 7*d*. which, for reasons explained at the last Annual General Meeting, represented an actual deficit of £2,763 19*s*. 10*d*. in comparison with the working of the previous year; at the same time it was shown that the Journal had grown by 691 pages, whilst the cost per page had increased from £2 4*s*. 8*d*. in 1919 to £2 9*s*. 3*d*. in 1920. Common prudence required the Society to raise the subscription, and the new rate coming into operation on January 1st, 1921, the accounts for that year show the income to have been £17,157 5*s*. 8*d*., an increase of £3,420 18*s*. 1*d*. As anticipated, however, the expenditure also has increased, amounting to £16,676 2*s*. 4*d*., and thus exceeding that of 1920 by £1,629 8*s*. 2*d*. Consequently, in spite of the expansion in revenue, the balance of income over expenditure amounts to only £481 3*s*. 4*d*., incidentally providing a complete justification for the Society's decision to raise the subscription.

The principal item contributing to the increase of income arises from annual subscriptions, these being £3,137 12*s*. 0*d*. in excess of those in 1920, the increase in life composition fees being only £42 as against the £931 10*s*. 0*d*. by which, in 1920, they exceeded those of 1919. The decision to raise the price of the Journal to the public from £3 to £4 is mainly responsible for an increase derived

from the sale of publications amounting to £509 4*s*. 1*d*. gross, although £79 11*s*. 7*d*. of this sum is due to expansion in sale of Annual Reports. One most unusual, but very welcome addition to the revenue is a gift of £10 10*s*. 0*d*. from Prof. W. J. Lewis, who, as a life compounder for over fifty years, loyally desired to assume a share of the heavy financial burden which the abnormal times have thrown upon the Society. Against these increases must be set a reduction of £204 in admission fees, new Fellows now paying £3 instead of £4, whilst the net proceeds from advertisements have diminished by £35 13*s*. 1*d*.

The increased expenditure is mainly on account of publications, the cost of printing the Journal having risen by £1,442 19*s*. 0*d*. owing to the continued expansion of the Transactions from the lowest point reached in 1918, as shown by the following synopsis:

	Number of Pages.		
	Trans.	Abstr.	Total.
1914	2,909	2,068	4,977
1918	995	1,032	2,027
1919	1,517	1,148	2,665
1920	1,648	1,708	3,356
1921	2,135	1,636	3,771

There is reason to hope, however, that one factor in this item has reached the zenith, the cost of the Journal per page during 1921 having been £2 12*s*. 4*d*. as against £2 9*s*. 3*d*. in 1920; but owing to a reduction in the charges for printing and paper, of which the full effect will be felt this year, there should be a substantial reduction in the cost per page for 1922. Further contributions to the increased expenditure were made by postage charges, £56 9*s*. 10*d*., authors' reprints, £84 0*s*. 6*d*. (the number of papers in the Transactions having increased from 182 to 243), Annual Reports, £246 5*s*. 3*d*. and furniture, £193 10*s*. 3*d*., a non-recurring outlay of £240 10*s*. 0*d*. having been made on bookshelves. On the other hand, there has been a reduction of £107 6*s*. 9*d*. in expenditure on stationery, and of £61 17*s*. 4*d*. on miscellaneous printing, whilst legal expenses, involving £261 5*s*. 0*d*. for 1920, were not incurred during 1921.

Thus it will be recognised that, in spite of the subscription having been raised, the working margin of the Society is very narrow if the prospective increase of the Journal to pre-war dimensions is kept in mind. The work of the Publication Committee is constantly showing that, in many cases, the abridgment of their communications by authors would offer the double advantage of presenting conclusions more attractively to readers and of saving much unnecessary expenditure on paper and printing. Another

source of economy, almost entirely in the control of authors and abstractors, relates to the charge for proof-corrections, which could be substantially diminished by making contributions in a form, preferably type-written, which does not require subsequent material alteration.

Whilst it has not been possible to make an addition to the invested capital during 1921, the increased rate of subscription permitted larger sums than usual to be placed on deposit in the first half of the year, resulting in an increase of £62 1*s*. 1*d*. from interest. Meanwhile, the improved value of trustee securities is reflected by an appreciation of £1,673 13*s*. 7*d*. in the market value of the Society's investments.

The following grants have been made from the Research Fund during the year:

	£	*s*.	*d*.
The increase in solubility of phenolic bodies in water on addition of a third substance. C. R. Bailey ...	5	0	0
(*a*) Preparation of aldehydes, (*b*) Condensation of *p*-nitrosodimethylaniline with alkylidene malonic and cyanoacetic esters. W. Baker ...	7	0	0
Studies in the anthracene series (continued). E. de B. Barnett	10	0	0
Physical properties of the higher normal fatty acids and their derivatives. W. H. Barrett ...	6	0	0
Study of certain fused reciprocal salt-pair systems. H. Bassett	20	0	0
Investigation of monothioethylene glycol. G. M. Bennett ...	5	0	0
Isomerism of the oximes (continued). O. L. Brady ...	5	0	0
A redetermination of the atomic weight of boron. H. V. A. Briscoe	20	0	0
Physico-chemical researches on some of the rarer metals and their salts. H. T. S. Britton ...	10	0	0
(*a*) Sulphurous esters of phenols, (*b*) Action of fuming sulphuric acid and allied reagents on paraffin hydrocarbons and their derivatives. G. N. Burkhardt ...	5	0	0
Biochemistry of iodine (continued). A. T. Cameron ...	15	0	0
Electro-deposition of metallic manganese. A. N. Campbell ...	10	0	0
Organo-derivatives of bismuth (continued). F. Challenger ...	10	0	0
Studies in ring formation. W. A. P. Challenor ...	15	0	0
Constitution of α-campholytic acid and of Willstätter's internal condensation product of ethyl methyldiacetylsuccinic ester. J. P. C. Chandrasena ...	15	0	0
Action of bases on the aliphatic disulphonic chlorides. J. B. Cohen	5	0	0
A study of the Reimer and Tiemann reaction extended to the aromatic hydroxy-acids. J. B. Cohen ...	5	0	0
Research on the tricarbazylmethane series. M. Copisarow ...	10	0	0
(*a*) New methods of preparing indole derivatives, (*b*) Influence of the entering group on the position assumed by a new substituent in benzene derivatives. W. Davies ...	20	0	0
A study of the effect of atomic volumes of *gem*-dialkyl groups on the ease of formation of carbocyclic rings. S. S. Deshapande	10	0	0
Experiments in halogenation (continued). S. N. Dhar ...	10	0	0
A study of the formation of four- and five-membered rings from substituted and unsubstituted carbon chains. F. Dickens...	10	0	0

	£	s.	d.
Investigation on the organo-tin compounds. J. G. F. Druce ...	6	0	0
Relation between chemical constitution and physiological properties of diazobenzeneimide and its derivatives. P. K. Dutt	10	0	0
Action of diazo-salts on sulphonamides (continued). P. K. Dutt	5	0	0
Compounds of the pyrylium series. A. E. Everest and A. J. Hall	5	0	0
The heat of oxidation of carbon over a range of temperatures. W. E. Garner	5	0	0
Production of organo-derivatives of thallium in the aromatic series. A. E. Goddard	7	0	0
Action of Grignard reagent on indium trichloride. A. E. Goddard	20	0	0
Synthesis of new associated dicyclic systems and the conditions governing intra-annular tautomerism. F. R. Goss	15	0	0
Optically active *sec*-octylamines and their relationships to the corresponding alcohols. S. Greenberg	15	0	0
The chemistry of bridged ring compounds exhibiting intra-annular tautomerism. R. C. Grimwood	10	0	0
The application of dibromoacetonitrile in organic synthesis. B. M. Gupta	15	0	0
Study of the alicyclic system containing two *cyclo*pentane rings having two carbon atoms in common. R. T. Holden ...	15	0	0
Investigation of 2 : 3-derivatives of *n*-butane. A. Houssa ...	10	0	0
Investigation of the catalytic activity of metal hydrosols. T. Iredale	15	0	0
An examination of the compounds of the hydrazobenzene group obtained by condensing picryl chloride with substituted phenylhydrazines. J. I. M. Jones	10	0	0
Influence of nitro-groups on the reactivity of substituents in the benzene nucleus (continued). J. Kenner	5	0	0
Study of bridged ring compounds. E. W. Lanfear	10	0	0
Researches on colloids (continued). J. W. McBain	20	0	0
Preparation and examination of some new tricyclic bases. T. S. Moore	20	0	0
Investigation of gallotannin (continued). M. Nierenstein ...	20	0	0
Studies in the chroman series. M. Nierenstein	15	0	0
Constitution of catechin (continued). M. Nierenstein	20	0	0
Preparation of *spiro*-hydrocarbons and their derivatives. W. S. G. P. Norris	15	0	0
A study of the effect of potentially quaternary carbon atoms on the ease of formation of carbocyclic rings. K. C. Pandya ...	15	0	0
Formation and stability of the condensed systems of *cyclo*-propane rings obtained from polyacetic acids of methane. W. J. Powell	15	0	0
Action of acids on metals. C. W. Rogers	5	0	0
Extension of benzoin condensation to unsaturated esters. C. Simpson	7	0	0
The effect of atomic volumes of *gem*-alkyl groups on the ease of formation of carbocyclic rings. B. Singh	10	0	0
The study of intra-annular tautomerism in the *cyclo*butane series. D. G. Smith	10	0	0
Formation of cyclic compounds from phenylacetaldehyde and cyanoacetamide. A. Stevenson	15	0	0
Reduction by metals in acid solutions. S. Sugden	6	0	0

	£	s.	d.
Coupling of diazonium compounds with esters of $\alpha\beta$-unsaturated fatty acids. G. Thomas	10	0	0
The mechanism of catalysis at metallic surfaces. A. F. Titley...	10	0	0
Preparation of nitrophenyl ethers of glycol, glycerol, and other polyhydric alcohols. H. Toms	10	0	0
Total	£629	0	0

This aggregate exceeds by £71 the sum of the payments made in 1920, and the balance of income over expenditure is only £18 10*s*. 5*d*. as against £123 1*s*. 4*d*. for 1920. The market value of the securities has increased by £1,073 3*s*. 3*d*.

A vote of thanks to the Auditors, proposed by the Treasurer and seconded by Dr. H. King, was carried, acknowledgment being made by Dr. G. Senter.

Dr. R. H. Pickard, in proposing a vote of thanks to the Treasurer, Secretaries, and Council for their services during the past year, referred to the great loss the Society had sustained by the death of Dr. H. R. Le Sueur. The motion was seconded by Dr. I. Smedley Maclean and carried unanimously, Sir William J. Pope making acknowledgment.

The President declared as duly elected the Fellows who had been nominated to fill the vacancies on the Council:

Vice-Presidents who have filled the office of President.—H. B. Dixon; P. F. Frankland.

Vice-Presidents who have not filled the office of President.—E. C. C. Baly; T. M. Lowry.

Secretary.—Irvine Masson.

Ordinary Members of Council.—(*a*) Town Members, *i.e.* those resident within fifty miles of Charing Cross: C. Dorée; J. J. Fox; J. R. Partington. (*b*) Country Members, *i.e.* those resident beyond fifty miles from Charing Cross: I. M. Heilbron; J. W. McBain; W. H. Mills.

Professor C. K. Tinkler, Dr. R. C. Farmer, and Professor T. S. Moore were unanimously elected to act as Auditors for the year 1922.

The President then delivered his address, entitled, "The Rôle of the Physicist in the Development of Chemical Theory."

A vote of thanks to the President, with the request that he would allow his Address to be printed in the Transactions, was proposed by Sir William A. Tilden, seconded by Professor J. Norman Collie, and carried with acclamation, the President making reply.

	£ s. d.	£ s. d.
To Subscriptions received in advance:— at £3 0 0		538 0 0
,, Sundry Creditors		*2490 10 8*
,, Research Fund:—		
As per last Account	15,369 12 4	
Add Excess of Income over Expenditure for the Year	18 10 5	
		15,388 2 9
,, Chemical Society:—		
Excess of Assets over Liabilities as per last Balance Sheet	*27,459 8 5*	
Add Excess of Income over Expenditure for the Year	481 3 4	
		27,940 11 9
		£46,357 11 2

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£6730 Metropolitan Consd. 3½ per cent. Stock A ...	7212 8 6	
£1050 London and North Western Railway 3 per cent. *Debenture Stock*	839 12 0	
£1520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£4341 Midland Railway 2½ per cent Preference Stock	3572 2 5	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923-53	1460 13 6	
£1200 North British Railway 3 per cent. Debenture Stock	1033 11 0	
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock, 1929/47	1995 0 0	
£1100 5 per cent. National War Bonds, 1929/47 ...	1045 0 2	
£2000 Registered 5 per cent. National War Bonds, 1927	2000 0 0	
£2000 Registered 5 per cent. National War Bonds, 1928	2000 0 0	
£600 4 per cent. Funding Loan, 1960/90	480 0 0	
		28,522 0 1
(Market *Value £21,078 11s. 3d.*)		
,, Sundry Debtors		*1719 3 0*
,, Subscriptions in Arrear £816 18*s*. Estimated to realise		630 0 0
,, Insurance paid in advance...		26 8 2
,, Cash at Bank		71 9 8
,, Cash in Hand		7 6
,, Research Fund:—		
Investments (value when acquired):		
£1000 North British Railway No. 1 4 per cent. Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock "B" Account	4587 18 0	
£1034 Great Western Railway 2½ per cent. Debentures	1049 15 11	
£1142 16*s*. 0*d*. New South Wales 3 per cent. Stock	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 0	
£1865 Midland Railway 2½ per cent. Debenture Stock	1010 0 9	
£806 Victoria 3 per cent. Stock	706 6 2	
£4498 11*s*. 0*d*. 5 per cent. War Stock	4267 4 10	
£300 National War Bonds 1928. 3rd Series	300 0 0	
		14,934 2 5
(Market Value £11,927 17*s*. 5*d*.)		
,, Cash at Bank		454 0 4
		£46,357 11 2

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B KEEN,
Chartered Accountant.

Approved { GEORGE SENTER, C. K. TINKLER, R. C. FARMER.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£	s.	d.	£	s.	d.
To Life Compositions				1585	10	0
„ Admission Fees				900	0	0
„ Annual Subscriptions :—						
Received in advance, on account of 1921	688	14	0			
„ during 1921 „ „	7845	8	0			
„ „ „ „ 1920	216	0	0			
„ „ „ „ 1919 and previous years	18	0	0			
	8768	2	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	260	0	0			
	8508	2	0			
Add Arrears at date: £816 18*s*.; Estimated to realise as per Balance *Sheet*	*630*	*0*	*0*	9138	2	0
„ Investments, Dividends on :—						
£6790 Metropolitan Consolidated 3½ per cent. Stock	235	11	0			
£1050 London and North Western Railway 3 per cent. Debenture Stock	22	1	0			
£1520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock	31	18	8			
£1400 India 2½ per cent. Stock	35	0	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	42	0	0			
£4341 Midland Railway 2½ per cent. Preference Stock	75	19	4			
£1200 Leeds Corporation 3 per cent. Stock	25	4	0			
£1500 Transvaal 3 per cent. Guaranteed, 1923/53	45	0	0			
£1200 North British Railway 3 per cent. Debenture Stock	25	4	0			
£700 Canada 3½ per cent., 1930/50	19	14	4			
£2100 5 per cent. War Stock	105	0	0			
£1100 5 per cent. War Bonds	38	10	0			
£2000 5 per cent. National War Bonds, 1927	100	0	0			
£2000 5 per cent. National War Bonds, 1928	100	0	0			
£600 Funding Loan, 4 per cent., 1960/90	16	16	0			
„ Income Tax Recovered	107	8	0			
„ Interest on Deposit	88	12	0	1113	18	4
„ Contribution, W. J. Lewis				10	10	0
„ Publication Sales :—						
Journals	2865	7	3			
Proceedings...	8	19	11			
Collective Index	61	5	1			
Library Catalogue	0	7	0			
Atomic Weight Tables	1	13	11			
Jubilee Volumes	0	2	6			
Annual Reports on Progress of Chemistry...	448	5	2			
Memorial Lectures (including Fischer Lecture)	16	9	5			
Gummed Abstracts	19	10	0			
Physico-Chemical Symbols	2	14	0			
	3424	8	3			
Less Publishers' Commission	323	10	1	3100	18	2
„ Proceeds of Advertisements in Journal	924	0	0			
Less Commission	55	4	11	868	15	1
„ Miscellaneous Receipts...				9	14	7
„ Donations to Library				406	5	0
„ *Subscriptions from other Societies*				23	12	6
				£17,157	5	8

FOR THE YEAR ENDED 31ST DECEMBER, 1921.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal :—						
Editorial Salaries	1008	0	7			
Editorial War Bonuses	208	7	6			
Editorial Postages	45	10	11			
Abstractors' Fees	754	10	0			
Printing of Journal	7408	10	11			
Banding	131	16	7			
Printing of Advertisements	305	19	4			
Wrappers and Addressing...	9	12	1			
Distribution of Journal	820	2	5			
Authors' Copies	352	0	10			
Insurance of Stock	16	4	0			
				11,060	15	2
,, Meetings, Hire of Hall, etc.				49	11	10
,, *Annual Reports on the Progress of Chemistry*				873	1	1
,, Purchase of Back Numbers of Journal				18	14	4
,, List of Fellows, Printing, etc.				144	10	1
,, *Library Expenses* :—						
Salaries	756	15	0			
War Bonus	298	0	0			
Books and Periodicals	409	9	5			
Binding	114	18	9			
				1579	3	2
,, Indexing for International Catalogue				7	10	0
,, Advertisements of Meetings				12	10	8
,, Donations :—						
Conjoint Board of Scientific Societies				5	5	0
,, Administration Expenses :—						
Salary of Staff	830	0	0			
War Bonus	332	0	0			
Wages (Commissionaire, Housekeeper, and Charwoman)	337	18	6			
War Bonus (Commissionaire, Housekeeper, and Charwoman)	114	8	0			
Coal and Lighting	96	15	3			
House Expenses and Repairs	110	2	2			
Telephone	15	2	2			
Furniture	253	19	6			
Tea Expenses	52	19	1			
Insurances	14	5	4			
Accountants' Charges	31	10	0			
Accountants' Charges (Balance, 1920)	10	10	0			
Commission on Recovery of Income Tax	5	7	6			
Miscellaneous Printing	220	12	0			
Stationery	189	5	10			
Postages...	208	5	8			
Miscellaneous Expenses	69	1	3			
Balance of Annual Dinner Account	14	14	11			
Carriage on Journals to Germany	18	4	0			
				2925	1	2
,, Balance being Excess of Income over Expenditure carried to Balance Sheet...				481	3	4
				£17,157	5	8

Research Fund Income and Expenditure Account for the Year ended 31st December, 1921.

Income.	£ s. d.	£ s. d.
To Dividends on :—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	14 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	154 0 0	
£1094 Great Western Railway 2½ per cent. Debenture Stock	18 1 10	
£1142 16s. New South Wales 3 per cent. Debenture Stock	34 5 8	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2	
£1365 Midland Railway 2½ per cent. Debenture Stock ...	23 17 9	
£806 Victoria 3 per cent. Stock	16 18 6	
£4498 11s. 0d. 5 per cent War Loan, 1929/47	224 18 6	
£800 *National War Bonds*, 1928	15 0 0	
		534 15 5
,, *Income* Tax Recovered		42 5 10
,, Repayment of Grants		99 5 11
,, Sale of Apparatus		5 0 0
		£681 7 2

Expenditure.	£ s. d.
By Grants	629 0 0
,, Travelling Expenses	7 12 0
,, Commission on Recovery of Income Tax	2 2 3
,, Advertisements	2 2 6
,, Longstaff Medallist (J. F. Thorpe)...	20 0 0
,, Engraving Medal...	2 0 0
,, Balance, being Excess of *Income* over Expenditure, carried to Balance Sheet	18 10 5
	£681 7 2

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 30th, 1922.

By SIR JAMES WALKER, D.Sc., LL.D., F.R.S.

The Rôle of the Physicist in the Development of Chemical Theory.

AT a time when the commerce between nations has emerged from the obscurity of custom and assumed paramount importance in the general mind, a scientific man may perhaps be pardoned if his thoughts take a commercial turn and incline to the consideration of the traffic between the sciences. As each country has its imports and exports with respect to other countries, so each science has its imports and exports with respect to other sciences. That there is a liquidated balance of trade can scarcely be maintained: one science remains a lasting debtor, another a lasting creditor. The commodities exchanged are ideas, with occasionally a method or an invention, and their value is not to be measured in depreciated sterling or more depreciated marks: what payment there is must be by way of barter. The general capital of ideas, methods, and inventions is ever increasing, and the accumulated stock is free to all who are capable of using it.

In this exchange the concrete sciences in general profit more than the abstract sciences. The pure mathematician is free from the trammels of matter or ether, and like the chimæra of old, bombinates joyously in a vacuum of n dimensions, shedding functions and operators in his gambols, which to the theoretical physicist may prove of incalculable value. The physicist in turn exports largely to the chemist, to whom the biological sciences, chiefly on their physiological side, are next indebted, and so on.

Since science is one, and is only split into separate disciplines to meet human dispositions and human limitations, the rise of borderland sciences becomes inevitable with the growth of knowledge. The practitioners of these sciences are middlemen in the exchanges; the mathematical physicist, the physical chemist, the biochemist, the physiological psychologist, and the like, facilitate the interchange of ideas and methods between the neighbouring scientific groups. A characteristic of contemporary science is the cultivation of these borderlands. Physical chemistry, if judged by the number of

researches it produces, or by the time devoted to it in academic instruction, now occupies a place almost coequal with the traditional subdivisions of chemistry proper. Since in what follows I shall have to distinguish as sharply as possible between physicists and chemists, I propose to divide physical chemists into two classes, according as their outlook is primarily chemical or primarily physical. For instance, Ostwald and van't Hoff belong to the first group, and these I shall call chemists; whilst Arrhenius and Nernst belong to the second group—these I shall call physicists.

We chemists are, I think, somewhat oblivious of the debt which we owe to physicists in the development of our science, particularly on its theoretical side. At the present time, the existence of the debt can scarcely be denied. The physicist is the scientific *conquistador* of to-day. He has crossed the interatomic ocean, he has skirted or explored the archipelago of electrons that fringe the atom, and has at last invaded the tiny continent of the nucleus. Invasion may seem too mild a term for his operations: he has hurled continent against continent with results that leave us aghast and filled "with a wild surmise" as to his future exploits. Such things are prominently before us, but we tend to ignore the less startling contributions of physicists to the advance of chemical theory during the last century, and these I propose to pass in brief review. We shall find the indebtedness to our physical colleagues so great, that it is no small consolation to know that a chemist and not a physicist laid the foundation of our modern science. As Bacon says, "There is an unavoidable necessity for men, if they will walk consistently, to have recourse to atoms, which are real, material, figurative, measurable things, having situation, resistanee, appetite, motion, emanation, and remaining for ever unshaken and the same amid the destruction and change of all natural bodies." This philosophical necessity was supplied by the atomic theory of Dalton, which welded the conceptions of atom and element into a coherent scientific system, and provided a simple quantitative symbolisation of even greater immediate value for the progress of chemistry than the parent theory itself. Indeed for many decades the atom, which the quantitative symbol originally represented, was practically forgotten, and only regained its significance in comparatively recent times.

Whilst the modern notion of the atom is due to a chemist, we owe to physicists the notion of the gaseous molecule as ultimate physically independent unit of chemical substances. Gay-Lussac, who may be regarded with equal right as chemist or physicist, since he was Professor of Chemistry at the *École polytechnique* and Professor of Physics at the Sorbonne, made a contribution of prime

consequence in the development of chemical theory by his discovery of the law of gaseous volumes. According to Dalton, all bodies, including gaseous bodies, enter into chemical action in simple multiples of their characteristic combining weights: according to Gay-Lussac gaseous bodies enter into chemical action in simple multiples by volume. There must then exist some simple relation between the volumes occupied by the combining weights of different gases. Dalton attempted to state the relation in the form that equal volumes of different gases contained the same number of atoms. This immediately led to contradictory results, and Dalton was induced to doubt the accuracy of Gay-Lussac's experiments. The reconciliation of theory with experiment was effected in 1811 by Amedeo Avogadro, Professor of Physics at the University of Turin, and independently a few years later by Ampère, also a physicist. Avogadro defined in effect the gaseous molecule and stated the principle that equal volumes of all gases under the same conditions contained the same number of molecules. These physicists were, however, so far in advance of the chemical thought of their time that their work, fundamental and simplifying as it was, fell into utter neglect. The reason is, no doubt, that volatile compounds were then comparatively few in number, that accurate methods of vapour density determination were not available, and that organic chemistry was not sufficiently advanced for the necessity of the precise definition of the molecule to be felt. The work of the great organic chemists of the forty years succeeding the announcement of Avogadro's principle led only slowly to the recognition of its significance. The French school of chemists, and Williamson in this country, saw the advantage of comparing equal volumes of gaseous compounds, but the systematic application of Avogadro's principle to organic and inorganic compounds alike was not made until 1858 by Cannizzaro, who first appreciated its full scope and bearing. By its use the present system of atomic weights was practically fixed, recourse being had in some cases, where volatile compounds were wanting, to the principle of the constancy of atomic heats, due to the collaboration of the physicist Petit with the chemist Dulong.

The next great principle, which we also owe to a physicist, is the law of the identity of the chemical and electrochemical equivalents. This law summarises the electrochemical work of Faraday, dating from the thirties of last century. The beginnings of electrochemistry are due to chemists—the practical side largely to Davy, the theoretical application of electropositive and electronegative in systematic chemistry to Berzelius. It was Faraday, however, who stated the quantitative laws of electrolysis and invented the nomen-

clature used at the present day. The quantitative association of matter with electricity is fundamental, and Faraday first gave precision to the ratio of charge to mass, of which so much has been heard in recent years.

By the end of the fifties the consideration of the organic molecule had led to the recognition of the essential quadrivalence of the carbon atom and its expression in graphic formulæ as we now use them. The molecule, from one point of view a mere gaseous particle, has now a definite structure assigned to it, a structure which can be represented by an easily grasped symbolism, dependent on the general notion of valency. In the next decade, progress was made in various directions, chiefly by chemists alone, but sometimes in association with physicists. First there was the development of the formulation of the carbon compounds which led eventually to the conception of the asymmetric carbon atom as put forward by Le Bel and van't Hoff, and to stereochemistry generally. Then there was the foundation of spectrum analysis by the collaboration of the chemist Bunsen with the physicist Kirchhoff. Here we have an example of the importance of a new instrument of investigation. The spectroscope of the physicist gave the chemist a method of detecting with ease and certainty quantities of chemical elements so small as to be beyond the reach of the finest balance. In its modern development, spectroscopy helps the astronomer on the one hand to state what substances are in the remotest stars, to measure their proper motion, and in general to determine the nature of the stellar universe, whilst, on the other, it enables us to peer into the structure of the atom. In the early sixties the spectroscope found its most striking use in promoting the discovery of new elements, for example, cæsium, rubidium, thallium, which without its aid would scarcely have been detected. In later times, the discovery of helium and all that it implies may likewise be attributed to the spectroscope.

With the definite establishment of atomic weights by the recognition of Avogadro's principle and the discovery of new elements it was only natural that a system of the elements based on atomic weights should be sought, and at the end of the sixties this received definite expression in the Periodic Law of Mendeléeff and Lothar Meyer. Almost simultaneously, the fundamental chemical law of mass-action regulating chemical velocities and chemical equilibria was laid down in a general manner by Guldberg and Waage, once more a co-operation between a chemist and a practitioner of a more abstract science.

The great contribution of the seventies to theoretical chemistry is to be found in the Phase Rule of the mathematical physicist, Willard Gibbs. It is a principle of the widest scope, applicable to

heterogeneous equilibrium, both physical and chemical. Being published in the Transactions of a minor academy and being, in addition, unattractive in form, it was only in the nineties that its vast importance was realised. Like Avogadro's principle, it was in advance of its time. Gibbs defined clearly the phases or mechanically separable constituents of a system, and the components of which the phases were constituted. By proofs based on thermodynamical principles, he showed that the number of phases in equilibrium could never exceed the number of components by more than 2, and that the system gained an additional degree of freedom for each phase short of this maximum number. The rule finds its most important application to solutions, which had only been investigated sporadically at the time of its inception. As instances of its utility on the great scale may be cited its application to the Stassfurt salt deposits by van't Hoff, and to the production during the war of ammonium nitrate from sodium nitrate and ammonium chloride.

Although much scattered work had been done on solutions in the seventies and eighties, it was only towards the end of the latter decade that a theory of any generality was reached. Van't Hoff, founding on experiments by the botanist Pfeffer, developed his osmotic pressure theory, according to which there is for dilute solutions a formal analogy between the dissolved substance in the solution and the same substance in the state of a gas. For gaseous pressure we substitute osmotic pressure, and find for dilute solutions the same simple laws as regulate the behaviour of gases. Although the principle is only a first approximation to exact statement, it opened the door to experimental and theoretical investigations which are still in progress. Amongst other things, it gave the theoretical basis for the determination of molecular weights of substances in solution by the freezing-point and boiling-point methods.

At first sight, electrolytic solutions could not be brought immediately under the osmotic pressure generalisation. The physicist, Arrhenius, however, by putting forward the theory of electrolytic dissociation almost simultaneously with the osmotic pressure theory, accounted for the exceptional behaviour of electrolytes in a simple manner. According to Faraday's theoretical conception, salts, acids, and bases in aqueous solution conduct electricity in virtue of their being split up into ions: Arrhenius gave a quantitative precision to this notion by showing how the actual conducting power was related to the number and speed of the ions (the relative speeds having been previously measured by the physicists Hittorf and Kohlrausch). Whilst the theory together with the law of mass-

action gives an accurate picture of the behaviour of aqueous solutions of feeble electrolytes, the treatment of strong electrolytes still offers difficulties which have not been overcome. Taking the theory of electrolytic dissociation as starting point, the physicist Nernst developed a comprehensive treatment of electromotive force, which to the chemist is not only useful in its application to determining very small ionic concentrations, but is indispensable in determining the affinities of certain systems. To Nernst also we owe a new thermodynamical rule of much use in calculating chemical equilibria and the affinities of the substances concerned in them.

We now come to a branch of chemistry the development of which has been almost exclusively in the hands of physicists. The phenomena of the discharge tube have always attracted the attention of investigators. Crookes considered that in high vacua the matter present was so tenuous and different in its properties from ordinary matter as to deserve the special name of radiant matter. The thought was a happy one, and the study of the passage of electricity through matter of such tenuity, where the effects of the electric strain on separate particles are not immediately wiped out by collisions, has led to discoveries which have revolutionised our notions both of atoms and of elements. Amongst physicists who studied such phenomena at the beginning of the productive period may be named Lenard Röntgen and J. J. Thomson. Not only was their work of great importance in itself, but it led to the development of experimental methods which accelerated the advance of knowledge to a marvellous degree. The electroscope here plays the part which was played half a century earlier by the spectroscope. Without this delicate instrument the quantitative study of radioactivity would have been practically impossible. The linking up of the investigation of X-rays, cathode rays, and radioactivity is one of the most interesting concatenations in the history of physical science.

The discovery of radioactivity we owe to the physicist Becquerel, and its successful prosecution to the combined activities of a physicist and chemist, Pierre Curie and his wife. The further development of the subject has been carried on by physicists and by chemists, either working separately or together, as in the instance of Rutherford and Soddy. The theory of atomic disintegration due to these workers breaks new ground in our conception of elements and atoms. The element is no longer an unchangeable ground material; the atom of Dalton is no longer an ultimate indivisible unit. The problem of the composition and structure of the atom assumes an insistent form : it ceases to be merely speculative, and demands a definite answer.

If the answer is to be more than qualitative we must attain a

knowledge of the magnitude of the atom. The beginnings of this knowledge were made in the middle of last century in the determination of a limit of continuity, for example, in gold leaf, in soap-bubbles, etc. The kinetic theory of gases, too, afforded information as to the probable magnitude of molecules, the relation of which to that of the atoms was definitely known. The study of the Brownian movement of suspended particles and the settling of suspensions enabled Perrin to estimate molecular and atomic magnitudes with some precision. The most accurate methods, however, depend on our knowledge of the fundamental electrical magnitude, the charge of the electron. In his Faraday Lecture, Helmholtz said: "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity." This conclusion follows from Faraday's laws of electrolysis, which show that "electricity" may be added to the list of chemical elements, obeying in its combination with other elements the laws of fixed and multiple proportions. If the elements of the ions are atomic, the electricity with which they are charged must be atomic likewise. We know accurately the ratio of charge to mass—say in the case of hydrogen, 1·0076 grams of which are associated in solution with 96,540 coulombs of electricity. If we could only learn then how many atoms of electricity it takes to make up 96,540 coulombs, we should know that there is the same number of atoms of hydrogen in 1·0076 grams of that element. To ascertain the magnitude of the charge of the electron or "atom" of electricity is of prime importance to chemists. The researches of J. J. Thomson, C. T. R. Wilson, Millikan, and other physicists have supplied the answer. We now know the absolute weights of the atoms with an error not exceeding 1 per cent.

Since the electron may be generated from any kind of matter, it was only natural that it should be regarded as a universal constituent of atoms. But as the electron is essentially negative, the atom must also contain positive electricity in order that it should be electrically neutral, and since likewise the mass of an electron is minute compared with that of the lightest atom, the main mass of the atom is in all probability associated with positive electricity. It remained then to determine, first, how the electrons were related to the positive part of the atom, secondly, how many electrons were contained in an atom. J. J. Thomson's first hypothesis that the electrons were distributed through a sphere of positive electricity uniformly occupying the whole bulk of the atom has been discarded in favour of Rutherford's theory that the positive electricity

is condensed in a single nucleus surrounded by electrons, the sum of the negative charges of which is equal to the positive charge in the nucleus. It was soon discovered from a study of the scattering of α-rays by the atom and the intensity of scattered X-rays that the number of electrons in an atom was comparatively small, being indeed about equal to half the atomic weight. The admirable work of Moseley on the characteristic X-radiation of the elements defined with certainty what we know as the atomic number of the elements, and it was an easy step to recognise in this essentially integral number the number of electrons surrounding the nucleus. Here we have definite material for the construction of an atomic model. For a given atom we know the nuclear charge and the number of electrons corresponding with it, and it only remains to find an arrangement of the electrons about the nucleus which shall correspond with known chemical and physical data.

In the atomic model of Bohr, the electrons move in orbits round the nucleus much as planets move round the sun; and on certain assumptions regarding these orbits Bohr has been able to calculate the wave-lengths of the spectral lines of the simpler elements with an almost uncanny accuracy. This type of atomic model satisfies the physicist, but it offers to the chemist no adequate account of valence. The chemist therefore naturally turns to the Lewis-Langmuir model, in which the electrons are ranged round the nucleus in successive shells and are regarded for schematic purposes as being at rest. That the electrons tend to form stable octets is taken as the fundamental principle in atom-building, and on this principle the main facts of valency may be accounted for. Only the electrons of the outermost shell are affected in chemical actions, and by suppositions as to the transference of such electrons from atom to atom, or the sharing of electrons between atoms, a moderately satisfactory picture of chemical combination and chemical compounds may be formed.

These two models, each satisfactory in its own sphere, are, however, irreconcilable: in one, the electrons move in orbits round the nucleus; in the other, they are fixed, or move about fixed points external to the nucleus. In science there can be no compromise in the strict sense, but only compromise in the sense in which a baby may be regarded as a compromise between its parents. It is to be hoped that these two apparently antagonistic atomic models may be the progenitors of a new atomic model which will satisfy physicists and chemists alike.

As has been said, it is only the electrons of the outermost shell that interest the chemist for his everyday purposes: they alone play a part in chemical reactions. The nucleus and kernel of the

atom are beyond the reach of his reagents. But the philosophical inquirer must not be limited to commonplace reactions. The nucleus is all-important for the explanation of radioactive disintegration. It is the nucleus which expels a charged atom of helium as α-particle, it is the nucleus which primarily expels an electron as β-particle, although in the end the outer electrons are thereby affected, with consequent changes in valence and chemical properties in accordance with the well-known scheme of Soddy and Fajans. As Sir Ernest Rutherford showed in a recent lecture to the Society, the nucleus of ordinary atoms is not immune from external attack, vigorous bombardment by fast α-particles leading in some cases to its disintegration.

The subject of isotopy is also primarily concerned with the atomic nucleus. The conception first arose in connexion with the radioactive elements, the scheme of disintegration leading to the necessity of acknowledging elements which differed in their radioactive properties (that is, in the behaviour of their nuclei) and were yet chemically identical. The powerful positive-ray method of Thomson, since modified by Aston and others, has shown that isotopy is far from being restricted to the radioactive elements, at least half the ordinary elements so far studied being, not simple, but mixtures of isotopes of different atomic weights. The atoms of such mixtures differ in their nuclei, but are identical in their outer electrons, and therefore in their chemical properties.

Theories of the structure of the nucleus are now based on the assumption that the nucleus of each atom is composed of hydrogen nuclei closely packed together with electrons. The weight of the atom is essentially determined by the number of hydrogen nuclei it contains, the positive charge of the nucleus (or the number of external electrons) is equal to the excess of hydrogen nuclei over electrons in the atomic nucleus. We have thus reverted to the hypothesis of Prout, promulgated more than a century ago, that all atoms are composed of hydrogen atoms, or rather of hydrogen nuclei. The "philosophical" atoms are therefore no longer the atoms of Dalton, but the electron, and the hydrogen nucleus or proton. Whether in these two there will be revealed an ultimate unity, we may leave without too much anxiety to the future.

We chemists have looked into the structure of the atom, not merely with the instruments, but with the eyes of the physicists, and to them again we are indebted for our knowledge of the structure of crystals. The work of Laue and of the Braggs on the refraction and reflection of *X*-rays by crystals has already yielded results of the greatest import. We know definitely how certain atoms and groups of atoms are arranged in crystals, and even the

arrangement of electrons in atoms does not seem beyond the scope of the method. An interesting side-light too has been thrown on colloidal solutions, it having been shown, for example, that the *colloidal particle of gold is crystalline and has the same crystal* structure as massive gold.

When we turn from the structure of the atom to the source of its activities we find another physical conception indispensable for its comprehension—the quantum theory of Max Planck. Originally proposed to account for the facts of radiation, this theory has proved a most powerful weapon of attack in physico-chemical problems of the most varied description: nothing seems beyond its range. It can be applied to the discussion of physical and chemical equilibria, to the atomic heats of solids, the molecular heats of gases, the absorption spectra of liquids, photochemical reactions, catalysis, and chemical action in general. It seems indeed to be a key which can open all doors, although the nature of the key is itself obscure.

Finally, we owe to the *all-pervading theory* of *relativity* the interesting suggestion that the difference between the mass of the hydrogen nucleus as found in other nuclei, namely 1·000, and the mass of the hydrogen atom, 1·0076, is due to the close packing of nuclei, the vanished mass having assumed the form of energy.

I fear that this recital of our obligations must have proved somewhat depressing to a chemical audience. Can we do nothing theoretical for ourselves? Within our special province we can and do. *The chemist's chief concern is, after all, with material change.* He has built up and is still elaborating a theory of the molecule, particularly of the organic molecule, which gives expression to the changes that occur when the molecule is being formed from other matter, or is being converted into other matter. But if the analysis of *properties and phenomena is to be carried back to pure dynamics* or electromagnetics, he is in the end dependent on the physicist, who is a specialist in these matters. This being so, are we content with acknowledging the *obligation*? Can we not in some measure repay it? One humble means of repayment is to provide the physicist with a variety of materials—pure materials—which he may study. But there is another of a much more fundamental character. By placing our theoretical requirements before the physicist we suggest to him new fields for cultivation, and provide a fresh stimulus to his research. This is a general method of repayment of the more concrete to the more abstract sciences. A firm *insistence* on the *fact* that no atomic model can be regarded as satisfactory by the chemist unless it accounts in a simple way for the phenomena of valency may guide the physicist to altogether new *conceptions*.

This repayment may strike even us as inadequate, but we have the satisfaction to know that if our wares are of comparatively little utility to the physicist, they are highly prized by the physiologist. The modern physiologist revels in colloids, osmotic pressure, and hydrogen-ion concentration, and thereby increases our activities by setting us problems which we feel bound to solve. Thus the exchanges between the sciences, although often one-sided, are always beneficial and foster the growth of science as a whole.

OBITUARY NOTICES.

GANESH SAKHARAM AGASHE.

BORN SEPTEMBER 15TH, 1886; DIED DECEMBER 2ND, 1921.

PROF. G. S. AGASHE, who died on December 2nd, 1921, was born on September 15th, 1886, at Bhivandi, Thana, Bombay Presidency. He came of the well-known Chitpawan, Mahratta race, and his father, the late Sakharam Rao Agashe, was well known in his circles for simplicity of life with advanced views. He received his early education at Ratnagiri and his University education at the Wilson and Elphinstone Colleges of Bombay University. After graduating with credit, he took up post-graduate work in the techno-chemical laboratories of the late Prof. Gajjar and obtained his M.A. degree in 1908. In school and college, Prof. Agashe was known to be clever and hard-working. Reserved by nature, he spent most of his time in the laboratory, in study and in thought. He had a passion for knowledge and he became Sir Mangaldas Nathubai Scholar at Owens College, University of Manchester, early in 1909. There he came under the influence of Prof. W. H. Perkin, jun., and Prof. H. B. Dixon, and took his B.Sc. degree in 1911. With Dr. Weizmann he worked on "Alcoholysis," which gave him his M.Sc. degree.

Agashe contributed, in the *Transactions*, "Condensation of Acid-Chlorides with the Ethyl Esters of (*a*) Cyanoacetic Acid, (*b*) Malonic Acid, and (*c*) Acetoacetic Acid;" and in *Science Progress*, "Stereo-isomerism and Optical Activity—a Critical Study, with a New Suggestion." After returning to India full of ideas for research work, Prof. Agashe entered the Madras University, as Professor of Chemistry at Pachaiyappa's College, Madras, in July, 1915. He wanted to form a research institute, but a change in the political condition of India, during the latter half of 1917, led him to leave the Madras University and he became

Principal of the newly-created National University at Adyar, Madras.

The claims of teaching and of organising the University left little opportunity for research, although Agashe has left a large number of data on adsorption phenomena, efflorescence, and deliquescence to be completed.

In May, 1920, he fell ill owing to physical strain, which developed into tuberculosis of the lungs. For a time he seemed to improve, but reaction set in and he succumbed to the disease in December, 1921.

Agashe was a young man, full of promise, impersonal and unemotional by nature and theosophical in ideas. He was the student's friend and President of the Second Students' Convention held at Madura in 1918. A beautiful casket was presented to him by the students of Pachaiyappa's College when he left for the National University, and this he gave to the new University.

Prof. Agashe's reading was many-sided, and he had a good grasp of mathematics, Sanskrit, biology, religion, music, logic, and history. As an educationist, he considered the present method of teaching in India faulty and he suggested what he called the "Evolutive" method. He planned editing a series of text-books on this method and inaugurated the same by an introduction: "Where We Stand in Science and How We Got There." Death overtook him before he could complete the work.

Before his death, Prof. Agashe made over his library, containing nearly four thousand volumes, to the National University. He leaves behind him his wife and his mother, as well as numerous friends and students to mourn his loss. T. S. N.

EDWARD WILLIAM TAYLOR JONES.

Born March 2nd, 1846; Died February 19th, 1922.

Edward William Taylor Jones died at his residence, The Oaklands, Wolverhampton, on February 19th, 1922, requiring but a few days to complete his seventy-sixth year. Until some twelve months before his death, in conjunction with his son, he was regularly engaged in his professional work, attending the laboratory daily, but failing health during the past year necessitated a break in his long activities, and he contented himself latterly with advisory help in the problems of his varied practice. Mr. Edward Jones, his father, was associated with that well-known Staffordshire iron master, S. H. Blackwell, whose name figures so frequently in the pages of Dr. Percy's book on "Iron and Steel," and who was a

pioneer in the application of science to the production of those metals. It may be that the prospects of the interesting and useful career that technical chemistry offered were thus early brought under his notice, and influenced him in the choice of his profession.

Mr. Jones was educated at a Wolverhampton private school, the principal of which was Mr. Tyrer, of whose qualities as a schoolmaster and a man, his son, Mr. Thomas Tyrer, was wont to give such pleasing reminiscences.

On leaving school, Mr. Jones entered the chemical works of Mr. J. H. Wildsmith, of Wolverhampton, but did not remain there long, as he was anxious to obtain better advantages for his chemical education than Wolverhampton offered at that time. He therefore proceeded to the Royal College of Chemistry, and studied under Professor Hofman, obtaining first class certificates in the various College examinations, and in the same year was awarded the silver and bronze medals by the Science and Art Department, taking first place in organic chemistry, and the fourth in inorganic chemistry.

In 1871, Mr. Jones returned to Wolverhampton to commence practice as an analytical and consulting chemist, and soon acquired a good *clientèle*. In 1873, be was appointed the first Public Analyst for Wolverhampton, and later in the same year to a similar position for South Staffordshire, whilst four years later the addition of North Stafford constituted him Analyst for the whole county. These positions he continued to hold until his death, and numerous other appointments as public analyst and official agricultural analyst were conferred on him.

The analytical methods for the control of food and drugs in the 'seventies were frequently crude and inadequate, and a reference to the early pages of the *Analyst* shows that disagreements, either in the analysis or the interpretation of the analysis, were frequent, the question of limits and standards, owing to inadequate knowledge, not having been settled. It was therefore a matter of justifiable pride that although he attacked every form of adulteration in these early days (he was the first to condemn the adulteration of American lard with cotton-seed oil) and had many references to Somerset House, and later, the Government laboratory, he never lost a case.

Mr. Jones was one of the founders of the Society of Public Analysts, and contributed numerous papers to its proceedings, dealing chiefly with methods of food analysis. He was twice a vice-president, and on two occasions personal reasons caused him to decline nomination for the presidency. He was also a Fellow of the Institute of Chemistry, serving for two periods on the Council.

Mr. Jones was a sound chemist, and an accurate analyst, well versed in the technique of his profession, and to these qualities he

added a fairness and a sense of proportion in interpreting his work that secured for him the confidence and esteem of his Authorities during his long period of service.

This brief notice would be incomplete without reference to one trait. He was always ready to place his knowledge and long experience at the disposal of a fellow Public Analyst, and many remember with appreciation the advice and help he gave them.

Mr. Jones leaves a widow, a daughter, and two sons, one of the last-mentioned having been in partnership with his father for some years.

H. S.

JOHN SPILLER.

Born June 29th, 1833; Died November 8th, 1921.

John Spiller, who died on November 8tb, 1921, was the oldest living Fellow of the Chemical Society, having been elected an Associate in 1857 and a Fellow in 1859. He was born on June 29th, 1833 and was therefore in his eigbty-eighth year.

As Spiller was a man wbo throughout his life loved to mix with his chemical brethren and as he was possessed of a personal charm that faithfully expressed the rare amiability of his character, and as he, moreover, retained, until nearly the end, something of the enthusiasm for new knowledge that is more often associated with youth than with age, he had a long succession of warm friends in successive chemical "generations."

Spiller acquired his first taste for chemistry at the City of London School, from which he passed to the Royal College of Chemistry, then under the direction of Hofmann, with whom, after going through the ordinary student's course, he remained for some time as an assistant teacher, being contemporary with, among others, Abel, Bloxam, and Crookes. After this, he worked at the Royal School of Mines, where in conjunction with Allan Dick and Riley he made a long series of analyses of British iron ores.

In 1856 he went to Abel as assistant ehemist in the Woolwich Arsenal, where he worked for twelve years, during which time his interest in photography led to his delivering lectures on that subject at the Royal Artillery Institution and the Royal Military Repository. He also lectured on Metallurgy at the Royal School of Gunnery, Shoeburyness. In 1868 he left the Arsenal to become chemist in the coal tar dye works of his brother's firm of Brooke, Simpson, and Spiller, where he remained for twenty years. During the remainder of his life his chemical interests were mainly those associated with photography.

To early volumes of the *Journal of the Chemical Society* Spiller contributed papers on "The Disguising Influence of certain Bodies in Detecting the Presence of Various Acids and Bases in Chemical Analysis" (Vol. X), "The Oxidation of India Rubber" (Vol. XVIII), "The Estimation of Phosphorus in Iron and Steel" (Vol. XIX), "The Weathering of Copper Ores" (Vol. XX), "New Sources of Ethyl and Methyl Anilines" (1873), and "The Occurrence of Native Calcium Chloride at Guy's Cliff, Warwickshire" (1876). A paper on "Platinum Silver Alloys" appeared in the *Proceedings* of the Society as late as 1897, and amongst the abstracts in the Society's *Journals* will be found records of communications to other journals on "The Identification of Coal Tar Colours" (1881) and on "The Composition of Ancient Mortar from a Roman Wall in London" (1889).

On photographic subjects Spiller was an enthusiastic worker and writer, one of his earliest papers (of which Crookes was joint author) appearing in the *Philosophical Magazine* of 1854 ("A Method for Preserving the Sensitiveness of Collodion Plates"), whilst a paper on "The Action of Chloride of Gold upon certain Salts of Silver" in the *Photographic Journal* of 1869 is of historical interest as foreshadowing the self-toning silver printing process. In the Royal Photographic Society he filled in turn every office, having been treasurer-secretary, vice-president, president, and editor of its journal.

Among Spiller's other activities, he was an enthusiastic volunteer in the early stages of the volunteer movement and received his commission in the 26th Kent Rifles as long ago as 1859—retiring, with the rank of captain, in 1877.

Spiller was twice married, first to Caroline Ada, daughter of the late Andrew Pritchard, F.R.S.E., and later to Emma, eldest daughter of the late Samuel Davenport, who, with their son, survives him, as do also a daughter and two sons of his earlier marriage.

B. D.

Ore Deposits and their Genesis in Relation to Geographical Distribution.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 8TH, 1921.

By JOHN WALTER GREGORY, F.R.S.

AMONG the common grounds of chemistry and geology is the study of the materials of which the earth is made, and especially of those minerals of which the use depends on chemistry, and the discovery on geology. It is the function of the chemist to show how these materials can be best employed, and of the geologist to point out how they can be most easily found.

These minerals are of two kinds—the earthy and the metallic—and in economic geology the term "metal" is used in its commercial or popular sense, and not in accordance with its chemical definition. The nomenclature of the miner and the mining geologist does not accept such elements as potassium, sodium, and calcium as metals, and therefore the crust of the earth is regarded as composed mainly of earthy minerals. The metallic minerals are predominant in the interior, where they form so large a proportion of the earth's mass that the quantity of terrestrial metals is ample. The bulk of the supply lies, however, at so great a depth that it is of no use except as a support to the crust and as the source of slowly ascending streams which have fed the veins of ores, and thus provided the metals essential to human welfare.

Many lines of evidence, including the weight of the earth, the distribution of radioactive materials, the passage of earthquake waves, and the analogy to meteorites, combine to show that the earth consists of a vast metallic core which is composed mainly of an alloy of iron and nickel, and which is enclosed in a comparatively thin shell of earthy minerals. The metallic core is the barysphere; the rocky shell is the lithosphere; and the most colossal metallurgical process that has taken place on earth was the settling down of the heavy metals to form the barysphere, and the floating upward of the lighter materials like a slag to form the lithosphere.

The rocky shell is now so thick that the metallic mass below is inaccessible and man is dependent on the minerals occurring within a few thousand feet of the surface. The useful metals are widely spread around the earth, but usually in quantities too small to be of service; they are present in sufficient amount to serve as ores only in far scattered localities.

The sporadic nature of the ores was the first fact that man

realised as to their distribution. "There is a vein for the silver;" the earth "hath dust of gold," says the authorised translation of Job; and early man knew to his cost that the veins of silver are thin and far apart, that the dust of gold is small and scarce, and that the tin needed for bronze was yielded only by a few remote places on the outer edge of the known world. This sporadic occurrence of ores is confirmed by modern experience, for although all the continents have their share of economic minerals, in each continent the mineral deposits of economic value occur in widely scattered mining fields; and in many of them all the ore is obtained from one body on one vein; whilst dozens of apparently similar veins and the bulk of the one producing vein may be barren of useful ore.

The rarity of minerals which repay mining is to some extent artificial, as only material above some particular grade of richness can be profitably worked; the minimum may be 60 per cent. of metal, as in some ores of iron; a mine may pay its way with 1 per cent. in a tin ore; or it may extract a dividend from material which contains only one part of metal in fifty million parts, in the case of a gold-bearing gravel which is favourably situated for cheap working by sluice or dredge. For all mineral there is a limit above which the material is a valuable ore and below which it is worth less than road metal.

Apart from such artificial commercial restrictions, there is an actual rarity of ores, which forced the early metal-using people of the Eastern Mediterranean to send to Cornwall for tin, to Spain and Armenia for copper, and to South Africa for gold. This far-flung distribution of ore deposits indicated their formation by some exceptional process and led early to speculations as to their genesis. The scientific study of ores began in Saxony on the famous mining field of the Erzgebirge. The Saxon mining pioneers realised three important facts regarding ore deposits: (1) their occurrence in veins ramifying through the ordinary rocks of the crust like veins in the body of an animal; (2) the frequent upward branching of the veins; and (3) the composition of the veins of crystalline minerals which indicated their formation at a high temperature.

The Saxon miners, in interpretation of their observations, founded the two rival schools of mining geology, the ascensionists and the lateral secretionists, whilst authorities on both sides held that ores were formed as metasomatic or replacement deposits. The Saxon miners anticipated the chief modern theories, although the points in common are concealed by differences in terminology. Bauer, writing in 1546, at a time when he had to defend his rejection of the astrologers' belief that the metals were due to changes wrought by the influence of the planets, attributed ores to ascending hot

waters, which deposited them in consequence of "the abstraction of the heat." Lehmann (1753) explained more fully that the ores are formed in the bowels of the earth, and that a lapidific juice rises like sap in vegetation in a great trunk stream, which on its ascent subdivides along branching rents like the bifurcations of a tree.

A great advance on this crude hypothesis was due to Lasius in 1787. He anticipated the modern view that, instead of this single trunk stream, ores are collected by widely diffused ascending water which leaches scattered grains of metal from the rocks traversed, and redeposits them in lodes at higher levels.

The fact that many lodes consist of successive layers of crystalline minerals naturally led to the view that they were deposited in fissures by hot water; but it was soon recognised that some veins were wider than any spaces that could remain open at their depth. Henkel, "the father of Mineralogical Chemistry" (1679—1744), explained such veins as due to the replacement, or, as he called it, the transmutation of the original rock. Von Trebra (1785) went farther and held that the veins were the ordinary country rock replaced by saline solutions, and he figured examples showing ramified, indefinitely bounded veinstones with features now accepted as characteristic of metasomatic or replacement lodes. Werner (1791)—the greatest of the Saxon school—repudiated the transmutation theories on the ground that "the intransmutability of the simple and elementary parts of bodies is one of the fundamental and immovable pillars of chemistry"; and, as he pointed out that some lodes thin out and become poorer as they are followed downward, he concluded that they must be filled from above and obtain their ores from material dissolved from the upper rocks by percolating water. Unlike his predecessors, Werner, to use the modern terminology, was a lateral secretionist, and not an ascensionist.

Revolt against these premature speculations led to the establishment of classifications based only on easily observed facts as to the shape of the deposits. Although this morphological system was founded in Germany, it was so generally adopted in this country that it has been often described as the British classification. This system has its advantages; it is simple, certain, and easily applied; whereas the genetic classification requires the elaborate study of each ore deposit before it can be assigned to its class. The morphological classification suffers, however, from the fundamental defect that, being merely descriptive, it is not suggestive; it summarises the known facts as to the form of a mineral deposit, but it gives no guidance as to the probable range and variations of that deposit in depth. The objection to Werner's system, that it was genetic and too theoretical, was to the feature which is now recognised as

its main merit. A classification, to be useful to the miner, must be a guide to future development. Hence modern classifications of mineral deposits are genetic.

Every mineral deposit must have been formed by one of four processes: (1) it may have solidified from molten matter as an igneous rock; (2) it may have been deposited mechanically by the breaking up of a pre-existing rock; or it may have been precipitated (3) chemically, or (4) organically from a solution derived from some older rock. Corresponding with these four processes, the genetic classification of minerals has four corresponding classes —the igneous, sedimentary, chemical, and organic.

Each of these four classes has contributed to the world's mineral deposits; but the extent of their contributions and the determination to which class certain ore deposits belong still provoke controversy, and are among the most active stimulants to research on ore formation. The uncertainty is not only regarding small deposits about which evidence is meagre; controversy has been especially vigorous over the greatest ore body now being mined, the iron lode of Kirunavaara, and the richest of all ore deposits—the Rand Banket.

The Igneous Ores.

In recent years, increased importance has been attached to the formation of ores by igneous agencies, and many great commercial ore bodies have been attributed to direct consolidation of molten magma like an igneous rock. The claim has been extended from metalliferous materials which have the characteristic structure of igneous rocks to solid masses of sulphide ores, such as the pyritic bodies of Rio Tinto, to sulphide impregnations and veins, such as the nickel ores of Sudbury, to the magnetite ores of North Sweden, and to some gold-quartz veins. This tendency to attach great importance to the formation of ores by igneous action is due mainly to the memorable series of papers by Prof. J. H. L. Vogt of Christiania. Under his influence the igneous ores are claimed to be of great variety and importance, as may be seen by reference to the text-book by Beyschlag, Vogt, and Krusch, for an excellent translation of two volumes of which we are indebted to Prof. Truscott. Vogt (1896) classified the igneous or eruptive ores into groups—"(1) deposits formed by 'magmatic differentiation'—that is, by the concentration of some metallic parts within the still fluid eruptive mass (magma)—and (2) deposits formed by processes subsequent to the eruption, such as sublimation (or in general pneumatolysis) and not cursive; fumaroles, solfataras, mofette, suffioni, geysers, and hydrothermal phenomena." Vogt regards many sulphides as well as oxides as due to formation within fluid magmas; he is

explicit that some sulphide masses should be included in the first group of his eruptive ores, for he said of the pyrrhotite gabbros that "the sulphides were formed during the cooling and crystallisation of the gabbro-magma, and that they were not formed by those pneumatolytic processes . . . but by the segregation of the ores in the molten rock itself. Pyrrhotite and pyrite are simply ordinary constituent minerals of the gabbro."

It is the members of the first of Vogt's groups which are the igneous ores; he regarded them as segregations of the metallic constituents in masses of molten rock; some of these segregations he attributed to gravity causing the fall of the heavier materials to the lower side of a reservoir or sheet of molten rock magma. As he said, differentiation helped by gravity splits magma to submagmata.

Vogt's other group, including ores formed by eruptive after-actions, such as pneumatolysis, hot springs, and solfataras, is *due to the action of superheated water, or perhaps gases, on the* rocks they traverse; and this second division of eruptive ores is hydrothermal in actual origin. The differences between the minerals formed as original constituents of a solidifying molten rock and those formed by the action of hot waters and vapours on an already solid rock are fundamental. Lindgren (1903), when throwing doubt on siliceous magmatic segregations, referred to them as possibly due to "eruptive after-effects . . . not to direct magmatic segregation," and he said that "the distinction between these two things should be emphasised. The latter takes place in a mass of fused material with or without the presence of a subordinate amount of water; the former involves entirely predominating aqueous solutions or gases." Vogt's clear separation of the eruptive ores from those due to eruptive after-actions has not always been maintained; and some later authors, whilst nominally accepting the igneous origin of the Sudbury ores, by their statements clearly show that they regard them as due to eruptive after-actions. "The term 'magmatic ore' is generally applied," say Profs. Tolman and Rogers (1916, p. 5), "to those phases of igneous rocks in which there has been *an unusual accumulation*, supposedly during the molten stage, of the accessory ore minerals." They say that "ores accompanied by destructive pneumatolytic action or those formed by hydro*thermal solutions are not to be classed as magmatic deposits*, although they may be closely related to, and follow the magmatic period." Nevertheless, they extend the use of the term magmatic beyond Vogt's first group, as they apply it to any ores segregated "under the influence of, or closely connected with, the molten stage of the parent rock."

This extension leaves the definition indefinite, and it is not the

sense in which ores were regarded as igneous or eruptive by Vogt and Coleman. Instead of the clear conception of Vogt of the ore being formed by direct magmatic consolidation, it depends on a vague, unspecified influence. If the term eruptive or igneous is to be applied to ores formed by pneumatolysis and by hot waters connected with or influenced by molten igneous rock, then nearly all ordinary lodes are eruptive; and Belt was right when he claimed the gold-quartz lodes of Australia as igneous injections.

Three terms have been largely used as the name of the class of ores formed by direct consolidation from a molten state, namely, "igneous," "eruptive," and "magmatic." The term "eruptive" was used by Vogt, but he later agreed with the objection raised in Beyschlag, Vogt, and Krusch, that it would include all pneumatolytic products. Vogt therefore subsequently adopted the term "magmatic," but if it be used to cover ores due to magmatic waters, it would include all those formed by juvenile waters, which are magmatic. If the class of magmatic ores includes all varieties from basic clots to veins formed by ascending juvenile water, it would be useless. Hence the older term "igneous" seems to me the best available, using it in its old sense for rocks consolidated from a molten magma and excluding the deposits of thermal waters, whether in fissures or springs. The old conception of "igneous," although out of date as regards its physical chemistry, expresses the fact that the fundamental division of both rocks and minerals is into the igneous and aqueous. It may be said that this distinction is only verbal, all magmas being solutions, and there being no essential difference between the deposition of a material from a solution cooling in a fissure and from a molten magma solidifying in a deep-seated reservoir. Until, however, the same term is adopted in practice for the liquefaction of iron in a furnace and in a bath of acid, geologists may be excused for retaining the terms aqueous or igneous. It is convenient to regard material which is fluid mainly through heat as molten, and material fluid mainly through reactions between its constituents as a solution. There is at least an essential difference between minerals that have solidified as primary constituents of a molten magma and those deposited from fluids circulating through fissures in a solid rock. Both materials may be magmatic; but the former set is due to magmatic segregation, which is an igneous process; the latter is produced by magmatic solution and is aqueous.

Adopting, then, as igneous those ores that comply with the definition of Vogt's first group of eruptive ores, there can be no doubt that such ores occur. The quantity of them that is at present mined is, however, very small. Some magmatic segrega-

tions of iron oxides, as at Tâberg, have been used in the past; others, like those of Routivaara and other masses of iron-rich basic rocks in northern Sweden, are vast reserves of iron that doubtless will be used some day; but these igneous materials are titaniferous magnetites, and as titanium is deleterious to iron and can only be eliminated during smelting by an extravagant expenditure of fuel, these iron-bearing rocks are of no present market value as iron ores. They are, however, magmatic segregations, and are as truly igneous as granite or basalt. Tâberg, south of Lake Wener in South Sweden, has a core of rock so rich in titaniferous magnetite that it contains a higher percentage of iron than some useful iron ores. This rock consists of basic felspar, olivine, and titaniferous magnetite, intergrown in relations explicable only by their direct consolidation from a molten mass. It is an igneous rock of the species known as cumberlandite, and it was long worked as an iron ore. It is chemically well known as the source of the discovery of vanadium by Sefstrom. A view of Tâberg was published in the *Philosophical Transactions* of 1755 as a mountain of iron. But despite its quality and its convenient position beside one of the main railways of Sweden, so that it could be cheaply mined, this cumberlandite has no present commercial value as an ore.

The claim that the igneous ores are of great commercial as well as petrologic interest depends mainly on the nickel sulphides of Sudbury and on the magnetite iron ores of Lapland.

The Nickel Ores of Sudbury.

Sudbury supplies a test case of the formation of igneous ores on an extensive scale.*

The general structure of the field, according to Prof. Coleman, is a great basin composed of a foundation of gneiss and granite, with a cap of sedimentary rocks, which would belong to about the same age as our Torridon sandstones, the ancient pre-Cambrian sandstones of the north-west of Scotland. Between the granite-gneiss and the sediments lies an igneous rock, which Prof. Coleman interprets as an intrusion wherein the heavier constituents sank to the lower part and there solidified as a norite, whilst the lighter constituents

* Mr. W. H. Goodchild has applied the segregation theory in a modified igneo-aqueous form to some analogous deposits in South Africa in a series of papers, "The Evolution of Ore Deposits from Igneous Magmas," in the *Mining Magazine*, 1918, **18** and **19**. A clear restatement of the igneous theory from the petrologic point of view is given by Dr. R. H. Rastall, *Geol. Mag.*, 1920, 290. The chemical principles have been restated by Prof. Vogt in "*Die Sulfid: Silikat Schmelzlösungen*," Pt. I, *Christiania, 1919*. The literature on the subject is now so voluminous that any adequate reference to it would be too lengthy for inclusion either in a footnote or an appendix.

collected in the upper part and formed a more acid rock, a micro-pegmatite. According to the igneous theory, the Sudbury nickel ore was formed by the similar gravitational segregation of the metallic constituents.

The view that the Sudbury nickel ores were formed when the norite in which they occur was still molten was adumbrated by D. C. Davies in 1888; it has been advocated especially by Barlow of the Canadian Geological Survey, by Prof. Coleman of Toronto, and by Prof. Adams of Montreal. The opposite view, that the ores were deposited by solutions in the norite after it had become solid, has been urged repeatedly, as by R. Bell of the Canadian Geological Survey, by Argalls, Emmons, and Dickson in the United States, by Posepny and Beck in Central Europe, by myself in 1907 and 1908, and later in Canada by Knight and Miller; but, as Knight remarked, "the advocates of the aqueous theory have heen 'like still small voices crying in the wilderness,'" and the igneous theory is still taught in most of the text-books and is doubtless still the orthodox view.

The claim for the igneous formation of the nickel ores rests on the following hypotheses: (1) that the nickel-eruptive rock is a vast sill-like laccolite thirty-seven miles long; (2) that in this laccolite the heavier constituents sank and formed the norite, whilst the lighter constituents collected in the upper part and formed the micro-pegmatite; (3) that this process of liquation by gravitation further led to the concentration of nickel sulphides at the base of the norite sheet, as masses of nickel ores; (4) that the nickel sulphide is a primary constituent of the norite; and (5) that the other minerals, especially the hypersthene, have been so little altered that the rock cannot have been much changed since its consolidation.

The statements of the case by Barlow and Coleman were very impressive, and my first doubts as to this explanation were suggested by some microscopic sections of the Sudbury ore which I had prepared to illustrate igneous ores in a teaching collection. These sections, to my surprise, were inconsistent with the igneous theory, but at first I attached little weight to them, as they had been cut from purchased material and might not be representative. The elaborate microscopic study of the Sudbury ores by C. W. Dickson (1903) could not be so easily dismissed, since his specimens are undoubtedly authentic, and representative of the commercial ore. His evidence proved that the sulphides in the ore were formed after and not before the silicates; that the sulphides were not deposited as a segregation in the molten magma, but in veins and fissures formed in the norite after it had become solid. The ore was therefore formed, not only after the consolidation of the norite, but even

after that rock had been shattered and fractured. Dickson's evidence has been strongly supported by the later studies of the Sudbury ore by Campbell and Knight, and also by Profs. Tolman and Rogers, who are most emphatic that the sulphides solidified after the silicates and by the replacement of the solid silicates.

The microscopic evidence seems absolutely fatal to the view that the sulphides are primary constituents of the norite. The distribution of the ores in the field, when examined closely, is also inconsistent with the igneous theory.

The view that the norite had been formed after the underlying granite, so that the sulphides at the Creighton Mine, for example, sank through the norite and accumulated in its basal layer above the already cool and solid granite, has been denied by C. W. Knight. He claims that this granite is younger than the norite. This view is supported by Tolman and Rogers's study of the micropegmatitic acid material within the ore and by the field evidence as to the relations of the granite to the norite. It was claimed by Mr. Barlow and Prof. Coleman that the ores occur along the basal edge of the sheet of norite, or in offshoots from it. At the Victoria Mine, on the contrary, the ore does not occur in the norite, but is completely enclosed by greenstones, which are altered basic igneous rocks much older than the norite. Thanks to Mr. Corless, I had the opportunity for a careful inspection of some exposures in this mine in 1908; and its evidence appeared to me absolutely inconsistent with the origin of the ore as a segregation within the norite, for the ore occurs in the greenstones.

Mr. C. W. Knight, after his detailed survey of the field for the Canadian Nickel Commission, reports that the ore is not confined to the norite and that the marginal ore bodies are for the most part outside the norite and indeed "rarely . . . in the norite," and there is only "a comparatively small quantity of commercial ore met with in this rock" [norite]. The Levack ore body, for example, is wholly in the granite-gneiss and is situated one hundred and seventy-five feet from the norite.

To emphasise this conclusion, Knight remarks, "it is repeated that the commercial ore bodies are found almost wholly in the rocks adjacent to the norite—not in the norite." The offset ore bodies, such as the ore-pipe at Copper Cliff and such mines as the Worthington, are explained by Knight as mineralised dykes, formed along earth-movements that shattered the rocks and admitted solutions which, circulating in the interspaces, cemented the fragments into a breccia by a sulphide cement. The one conclusion which he declares (1917, p. 113) is a "certainty is that the

sulphides were introduced after the norite-micropegmatite had solidified. This is proved beyond doubt."

In recent years, the trend of opinion appears to have set against the view that the Sudbury ores are primary segregations, and towards the explanation that they are due to processes acting after the solidification of the eruptive rocks. Barlow admitted, in the reprint of his memoir (1907, p. 123), that he had laid too much emphasis on magmatic differentiation, as other agencies in addition "have contributed rather largely," including the action of heated solutions "in dissolving out, and . . . redepositing these sulphides." Hence Barlow practically abandoned the theory that the ores were due to igneous consolidation, and attributed them to the deposition of matter carried to their present position in solution. Some later authors attribute the ore to the after-actions of the norite intrusion, or to segregation in some deep-seated reservoir, but not in the norite-micropegmatite laccolite. On this view the differentiation between ore and norite took place before the norite reached its present position; if so and if the sulphides were formed after the silicates and were introduced in solution, the ore was not formed by consolidation from a molten state, and was not igneous in formation. It may be due to magmatic waters, but not to magmatic segregation. It is aqueous—not igneous.

The Iron Ores of Lapland.

The iron ores of Swedish Lapland afford the other leading case of an important ore now generally regarded as an igneous rock. They are of three chief types—the vast magnetite sheet at Kirunavaara with less than 1 per cent. of titanium, the magnetite masses in the gneiss of Gellivaara, and the titaniferous magnetites (titano-spinellite) in the gabbros at Routivaara.

The ore bodies of the third type, despite their vast bulk, are of no present economic value owing to their low grade and high percentage of titanium. The Kirunavaara and Gellivaara ores, on the other hand, supply important mines and are both claimed as due to magmatic segregation. The Kiruna ore body has attracted most geological attention, probably because the associated rocks are less altered than those of Gellivaara. It is natural therefore to turn to Kiruna for the simplest interpretation of these ores.

The Gellivaara problem, however, seems to me the simpler. The ores there are masses of magnetite in a biotite-gneiss; at the time of my visit the footwall of the ore body was exposed at three of the mines in a large, even fault plane, by which the ore is sharply bounded; the upper margin of the ore, on the contrary, is very irregular, and there is no sharp separation below the ore and decom-

posed iron-stained gneiss; here and there within the ore body occur blocks of gneiss which also pass gradually into ore, and as their foliation is parallel to that in the adjacent gneiss they are in their original position. The ore has grown around them. The Gellivaara ore bodies show the features which have led to the conclusion that the iron ores of the north-west of England have been formed by replacement. The ores of Gellivaara appear due to descending solutions which have dissolved iron from the ferruginous minerals in formerly overlying country rock and have deposited it where the descent of the solutions was stopped by some impermeable surface.

The Kirunavaara ore body has a very different story. The ore is enclosed within unfoliated igneous rocks; Löfstrand in 1892 therefore suggested that it had been formed by segregation within a molten magma like the iron ore at Tâberg. The underlying rocks are syenites passing up to a syenite-porphyry containing nodular, spherulitic, and flow structures which are generally regarded as evidence of volcanic origin. Above the iron ore occurs a series of quartz-porphyries, in which the evidence of volcanic action is still more conspicuous, and includes abundant spherulitic bands, altered glass, and interbedded tuffs. Above the quartz-porphyries lie sedimentary rocks, including more volcanic tuffs. There is strong evidence that the ores were formed after the eruption of the syenite-porphyry and at least in part before that of the quartz-porphyry, for abundant pebbles of different varieties of the ore occur in the overlying quartz-porphyry. These pebbles have been regarded by most geologists who have examined them in the field as fragments of the Kiruna ore, and as proof that the ore was formed before the quartz-porphyry.

Such are the primary facts by which the theories of the formation of this vast deposit of iron ore must be tested. There have been two main lines of explanation—the igneous and the hydrothermal. The igneous has been advanced in four different forms. (1) The first was the direct origin of the iron oxides during the consolidation of a molten mass; but that view became untenable when it was found that the rocks on the two sides of the ore were formed at different dates. (2) Prof. R. A. Daly (1915) has reintroduced the direct magmatic origin of the ore, which he explains as formed by the segregation of the iron oxides of the quartz-porphyry by subsidence under the influence of gravity. The quartz-porphyry, however, contains only 4·8 per cent. of iron oxide, so that it is not a likely rock to produce so colossal an ore body by liquation. Moreover, it was discharged in successive flows, so that liquation could only collect ore at the base of each sheet. Again, as the quartz-

porphyry contains titanic oxide, any iron ores thus formed should have been titaniferous magnetites, and not an ore low in titanium. The earthy mineral found at Tåberg is a felspar, and a felspar would be the natural silicate to occur with the Kiruna ore if that material were due to consolidation from the magma of either the syenite- or quartz-porphyry; but the earthy mineral is apatite, and the massive varieties exhibit structures (for example, Geijer, 1910, p. 110; compare, however, p. 258, rejecting this explanation) which favour its formation by replacement of a lava. Phosphate of lime often retains the structure of the materials that it replaces with such perfection as to leave no doubt of their original nature. Some of the Kiruna apatite was formed by the replacement of an igneous rock with a well-developed fluxion structure, and was not an original constituent of the porphyry. (3) The third variety of the magmatic hypothesis is that of Stutzer, who maintains that both the underlying and overlying porphyries are intrusive rocks and not lava flows, and that the ore was injected as a magmatic dyke—an igneous rock of ultra-ultrabasic type. (4) Per Geijer (1910), in his valuable account of the geology of the field, also holds that the ore was introduced in a molten condition; he explained it as a lava flow discharged in the interval between the two series of porphyries. Lava with 60 per cent. of iron oxide is not a very plausible material. So in a later paper (1918), Geijer withdrew this suggestion and accepted Stutzer's theory that the lode was intruded as a sill. His former view seems, however, more consistent with the field relations of the ore, and little less difficult of belief as a matter of physical chemistry.

The alternative to the igneous theory represents this ore as formed on the surface of the syenite-porphyry by deposition there of iron oxides leached out of the underlying rocks. The iron might have been dissolved either by meteoric waters and deposited as a bog-iron ore or laterite, or, as urged by Bäckstrom, by hot waters rising from the cooling lava. Bäckstrom's view adopts water at a high temperature, and has generally been known as the pneumatolytic theory; but as the action was near the surface and probably at a moderate temperature, and as tourmaline has been found only once in the ore, the process (despite the abundance of apatite) would appear more suitably described as hydrothermal.

De Launay has supported Bäckstrom's hypothesis, with the modification that the process was hydrothermal rather than pneumatolytic. (Herdsman's theory belongs to the same group.)

This origin of the ore seems to me indicated by the following facts:

(1) The ore lies along an horizon separating rocks of two different ages.

(2) Between the ore and the normal syenite-porphyry occurs a band of altered iron-stained porphyry, into which the ore passes by a gradual passage.

(3) The upper or hanging wall of the ore is sharper than the footwall, and in places along the latter altered syenite débris occurs mixed with ore.

(4) The ore is not titaniferous magnetite; the Kiruna ore contains about 0·31 per cent. of TiO_2, whereas that oxide is abundant in the syenite. If the iron ore had been formed as a molten segregation in the syenite-porphyry, it should have had a much higher percentage of titanium; whereas if concentrated by solution, an iron oxide low in titanium would have been the natural result.

(5) The ore includes some "stratified" ore which retains fluxion structure, although the material has been altered to apatite—as part of a replacement process.

(6) The ore is shown to have been formed earlier than the quartz-porphyry by the ore fragments in that rock.

It seems to me, therefore, that of the iron bodies of Lapland, although Routivaara is a mass of igneous rock rich in iron, it is not yet an iron ore; that the ore bodies of the Gellivaara type are *metasomatic formations due to descending meteoric waters* like many of the ore bodies of the Lake Superior region; whilst the ore body of Kirunavaara was formed by the redeposition of iron oxides dissolved out of the underlying syenite-porphyry, and was to some extent enlarged when hot solutions bearing phosphoric acid replaced part of the lava by banded apatite, formed in it some crystalline apatite, and deposited apatite veins in the overlying quartz-porphyry.

Pyritic Masses.

The igneous origin of sulphide ores has been advocated by Vogt (1899) for the great pyritic masses, of which the classical examples occur in southern Spain at Rio Tinto and Tharsis, on the ground that their solidity and homogeneity presented difficulties to their formation as ordinary lodes. In extreme opposition to this view was that of E. D. Peters and others, who claimed these pyritic bodies as lake deposits. The similar pyritic mass at Mt. Lyell, Tasmania, has been formed as a replacement mass by solutions permeating a block of strata which had been completely shattered between intersecting faults; in advancing that explanation for the ores of Mt. Lyell, I remarked (1905) that it appeared also applicable to the Spanish examples, as judged from the monograph by Gonzalo of Tarin (1888), and that explanation has been adopted by Finlayson (1910) in his valuable account of the Spanish pyritic mines.

The Aqueous Ores.

The great bulk of ores has been deposited from solutions; and owing to the infinite variety of conditions which control the circulation and decomposition of solutions, lodes are extremely varied in type, and the classifications of lodes have become very complex. The complexity has become so great that the classifications break down in a bewildering number of subdivisions which overlap with others that are assigned to distant sections of the same scheme.

At present there is a widespread tendency, as illustrated by Lindgren's "Mineral Deposits," to divide the chief ores into groups based on depth of origin, adopting three classes—deep, intermediate, and shallow. This plan appears sound as concerns the superficial ores; but the subdivision of the intermediate and deep-seated ores is less well marked, and this part of the classification may prove only of temporary service.

The authors of the earlier systems agreed in their desire for one universal explanation of all ore deposits; that was the Holy Grail for which all the metallogenists were in quest. Most of the first students of ore formations were ascensionists, and although Werner supported the opposite view by weighty arguments, such metals as gold, silver, lead, and copper appeared so much more likely to be derived from the deeper than from the upper parts of the crust that the ascensionist theory long remained predominant.

The lateral secretion view was readvanced in 1854 by Bischof, who explained the supposed absence of the metals from the surface rocks by the hypothesis that they occur in quantities adequate to supply the lodes by slow concentration, but too small to be detected by ordinary chemical analysis. Bischof's pupils sought to establish his theory by the discovery of the ore metals in the sedimentary rocks; but their results were inadequate as a general support to the theory until F. Sandberger undertook a detailed study of the rocks, ores, and veinstones of the Black Forest (Schwarzwald) in order to demonstrate the derivation of the lodes from the rocks they traverse. He soon established the close connexion of the veinstones and the country rocks, but at first he failed to find in these rocks any of the lode metals. The possibility occurred to him that the lode metals might be restricted to the rarer mineral species present in the rocks; so he collected from various rocks quantities of their less abundant constituents, and analysed them. He then found that the micas and the ferromagnesian minerals contain small but persistent quantities of such metals as copper, lead, zinc, cobalt, nickel, antimony, etc.

Sandberger applied his method to the older rocks of many districts and generally found in them small quantities of the same metals. After this discovery the lateral secretion theory leapt into popularity, which was extended when S. F. Emmons gave it his moderate but influential support, and Sonstedt's claim to the detection of gold in the water of the Irish Sea made lateral secretion a possible explanation of gold ores. Sandberger's discoveries, it was claimed, rendered unnecessary any appeal to inaccessible depths for the metallic constituents of lodes. The substitution of a visible and accessible source of a material for one which must remain hypothetical and inaccessible is generally welcomed; and Sandberger's discovery having removed the chief argument against lateral secretion, that doctrine was accepted with enthusiasm.

Magmatic Waters.

The widespread adoption of the lateral secretion theory was doubtless encouraged by the long-prevalent belief that all the water on the earth's surface is of meteoric origin. The possibility that any water is derived primarily from below (that is, is plutonic, or magmatic, or juvenile) was emphatically rejected. If no water comes from below, and lodes are aqueous in origin, then all the metals in lodes must have been collected by water from the upper layers of the earth's crust.

For some reason the possibility of magmatic water was regarded as the most reprehensible of geological heresies. The existence of such water was denied by chemists and engineers; it was not until the hot waters that broke into the Simplon Tunnel proved to be free from chlorine that the existence of juvenile waters was generally acknowledged. The ascent of this water is widespread and continuous, and the quantity added to the surface waters in long periods of time must be enormous. The increase in the volume of the oceans since early geological ages may be explained by the constant upwelling of magmatic water.

The acceptance of these widespread ascending waters has sapped the predisposition toward the lateral secretion theory; and geologists generally accept Stelzner's claim to have shown that the metals found by Sandberger in the accessory minerals were not original constituents, but were introduced in solution. They are, in fact, secondary, like the lode metals, and not primary, like the iron, magnesium, and aluminium of the ferromagnesian silicates.

The recognition of magmatic waters explains the general association of ores with igneous rocks. Where crustal movements have enabled the igneous rocks to reach the surface, the accompanying

nagmatic waters have risen above them or through the fractures eside them. The function of the igneous rocks has been neither o act as the source of the metals, nor as the "thermosphere"—o use Le Conte's phrase—to supply the heat; but they act as a unch which, being forced upward, fractures the crust and thus nables the superheated metal-bearing waters to rise from the deeper ayers of the lithosphere. These solutions are of various types and ualities. Hot waters charged with boric and fluoric acids act as neumatolytic agents and deposit ores of tin and tungsten, produce ems by the solution and reprecipitation of alumina, and alter ranite into stocks of china clay. Superheated water is the ordinary ydrothermal agent; where it rises from an intrusive igneous ock and permeates the adjacent zone, it produces contact ores; vhere it rises through fissures or along permeable lines through the rust, it deposits its earthy and metallic constituents in forms lependent on the spaces into which it enters and on the precipitating gencies it encounters.

There is no need here to consider the various classifications of the queous ores, with their multitude of subdivisions, but I desire to mphasise two principles involved: (1) the essential unity of the vhole series of processes; (2) the importance of the distinction etween the primary ores formed by ascending waters and the econdary ores due to the action of meteoric water descending or irculating laterally through the upper rocks of the crust.

Geologists have found it convenient to subdivide many phenomena nto the epigene and the hypogene; and the same treatment is nstructive in the study of ores. The hypogene ores include the rimary ores and those ore-producing materials which have been alled protore. All rocks are potential supplies of mineral matter; nd therefore, according to the standard definition of the term, are rotores. The iron of a basalt may be concentrated by weathering nd thus form a sheet of ironstone; so basalt is a protore of iron. In aluminous rock may be decomposed to bauxite and so is a rotore of aluminium. A solution rising up a fissure may have ll its salts deposited in local concentrations by meeting with some recipitant, or by being retarded in its ascent; in such places it vill form ore, but elsewhere the deposition of its material may be o slow and widespread as to form only protore. But when the ountry enclosing a vein of protore is lowered by denudation, the vein s worn down and its metallic constituents are dissolved and redeosited in the layer below. This process continued adds the metals rom two layers to the third layer of protore; and they in turn are arried down by the lowering of the surface and cause the enrichment f the top of the vein below the surface. The rich ore bodies which

have been the great prizes of the mining industry and the most valued treasure-houses of the mineralogist are mostly due to this process of surface or sub-surface enrichment. The explanation of these "bonanzas," the warning that a sudden fall in value from ore to protore may be expected in conditions favourable to such enrichment, and the encouragement that after the sudden fall in value the ore may continue to great depths with only a slow further reduction in grade are among the most useful guidance which geology has offered to the metal miner.

The Rand.

The Rand goldfield has been claimed as an exception among the aqueous ores, since its gold has been attributed to the action of solutions which have left no trace of their planes of infiltration. These planes should surely have been discovered if they ever existed, for the exposures on the Rand are most extensive; and the carefully compiled sections showing the variations in the nature and values of the gold-bearing beds are the most complete and extensive in mining records.

The rocks of the Rand goldfield are mostly interbedded slates, quartzites, and conglomerates which have been bent into a broad basin and have been injected by numerous dykes and sills. The rocks belong in age to the later part of the pre-Palæozoic. The gold ore consists of beds of coarse conglomerate that were formed as gravel or shingle. Hence the first explanation represented the ore as a placer deposit. It was soon found that the gold is not in the quartz pebbles, but in the cement between them; but although that fact is in striking agreement with placer deposits, it was regarded as fatal to the theory, and others were proposed. The main rival to the placer theory is that the gold has been introduced in solutions as in ordinary lodes, and that the solutions circulated through the conglomerates because they were more permeable than the adjacent sandstones.

The placer theory was advocated by Becker, who refuted the argument based on the supposed greater permeability of the conglomerate. But serious difficulties to the first statements of the placer theory led to its general rejection. A visit to the Rand in 1905 supplied what seemed to me adequate explanations of these difficulties, and further evidence in favour of the placer theory, which I advocated in a paper to the Institute of Mining and Metallurgy in 1905. The discussions then showed how strongly that conclusion was opposed to current opinion; but as Dr. E. T. Mellor, on behalf of the Geological Survey of South Africa, has adopted that theory after several years of detailed study of the

Rand, it is now the official view. Mr. C. B. Horwood has defended the filtration theory in his book on the Rand goldfield; but the trend of opinion appears to have set in favour of the placer theory.

That theory is consistent with the general conditions under which the ore is found. It consists of beds of quartz-conglomerate, which were laid down on the margin of an area composed of granite injected into a schist; these schists were traversed by quartz-veins which were doubtless auriferous. The denudation of this land provided the material for the sheets of clay, sand, and pebble beds, and for layers of iron sand which were deposited along the coast. This series of deposits was subsequently injected by many dykes and silicified. The dykes are occasionally associated with sudden changes in ore value; but the variation in the mineral contents of the conglomerate is usually so independent of the dykes as to render it most probable that the exceptions are due to coincidence and faults.

The gold in the rich conglomerate differs from that in typical river placers, as it occurs in very minute particles; in river deposits such small gold would be scattered through thick beds of silt, and form a very poor ore. Its concentration into rich ore on the Rand may he explained by long-continued tidal action; the wash of the tide to and fro would sweep away most of the silt, and leave a concentrate of the heavier particles in the hollows between the larger pebbles. These positions served as natural riffles in which long-continued wash of the tide would collect the gold in rich deposits in spite of the minuteness of the particles. The gold is rarely in nuggets, although a few have been recorded from Riet-fontein up to 2 oz. in weight. As a rule, the gold occurs in minute particles, as in those placer deposits which are formed from lodes in which the gold is finely disseminated. The minerals associated with the gold are those usually found as grains in sedimentary rocks, such as tourmaline, rutile, zircon, and apatite; the ore also contains detrital diamonds, and those characteristically alluvial metals—platinum and iridosmine.

Of the earthy minerals, the most typical silicate present is a chloritoid—a mineral characteristic of pressure metamorphism, and not of veins deposited from solution. The absence of the sheets of secondary vein-quartz is a feature unlike lodes formed by solution.

The most conspicuous metallic mineral in the banket is pyrites, which often occurs in bands, as if formed from patches of black iron sand by conversion of the iron oxide into sulphide. Some of the pyrites has naturally been formed by the replacement of quartz.

Emphasis has been laid by Horwood on the fact that the gold in the banket contains up to 10 or 12 per cent. of silver, and therefore

cannot be placer gold, as that is much purer. This argument would not carry conviction to a placer miner, who has to be content with £2 10s. per ounce for his gold, owing to its containing 50 per cent. of silver. The fact that the Rand gold contains 12 per cent. of silver is no objection to its placer origin.

The Rand ore agrees in its essential features with placer deposits, and differs from lode formations by the lack of infiltration channels and of the extensive hydrothermal alteration accompanying rich ore due to solution.

Conclusion. Ore Distribution and Mineral Provinces.

For mineral deposits in general the distinction that seems of primary importance is between the epigene and hypogene formations. The epigene series includes those formed near the surface, such as coal, oil, oil shale, salt, bauxite, some china clay, and phosphates, and among the metallic ores all placer deposits, and gossans, most ores of iron, manganese, and mercury, and the rich patches of gold and copper due to surface and sub-surface enrichment.

The hypogene formations include the lower portions of all the ordinary lodes, the rich ores found in deep shoots, the low-grade primary ores of innumerable veins, pipes, and domes of china clay, veins and seams of apatite, mica, and graphite, and the scattered grains of chromite. Of the epigene materials, the distribution is dependent partly on the underground sources of supply and partly on the climatic agencies which control various biological and chemical processes. The gossans and placer deposits are dependent on local supplies of metals; and most metalliferous mining fields are in or near areas of eruptive activity.

The association of ores and eruptive rocks is so general that in the exceptional cases geologists are often led to regard the presence of the ore as in itself indirect evidence of former igneous activity. Thus, to account for the lead and zinc ores of the Mississippi, it has been urged repeatedly (for example, by Pirsson) that there must be igneous rocks underground, in spite of the sub-adjacent water-logged beds which, as remarked by Mr. Foster Bain, would protect the overlying rocks from the entrance of ascending hot waters.

The study of the distribution of the economically useful minerals and the delimitation of metallogenetic provinces depends on correct interpretation of the chemical processes by which the minerals were formed. Maps of the distribution of ores throughout the world throw little light on ore genesis unless they distinguish mining fields of different ages, or the products of successive mineralisations.

The magmatic segregation of ores appeared at one time to offer the most likely explanation of the sporadic distribution of ore fields,

and of the existence of mineral provinces. The mining fields were thought to occur above local concentrations of ore due to magmatic segregations in the undercrust. The local occurrence of ores may, however, be explained by elevations of the barysphere haviug raised rock material rich in metals near the surface. These subterranean domes of the barysphere would be local areas of high temperature and would be normally surrounded by fractures which would admit lode-forming solutions into the upper crust. The major elevations of the harysphere are probably due to the deformation of tbe earth as it cools and shrinks. The cooling is continuous, but the resultant deformation is doubtless periodic. Lode formation takes place especially at epochs of major disturbance of the earth's crust, and in those belts where the crust is most fractured, along mountain uplifts and on the borders of the great sunklands.

The disturbances of each successive world-wide crustal deformation are arranged on a regular plan, which there is much evidence to show is tetrahedral. Four large areas of subsidence are antipodal to four areas of uplift; the uplifted and sunken areas are separated by six belts of folds and fractures, along which ore-formation has taken place at intervals.

The nature of the primary ores along these belts is dependent on the natnre of the fractures and their depth. The simplest plan of ore distribution is that of the mercury ores. The chief mercury-fields are in Spain, Italy, Idria in South-east Austria, California, and Peru; they are all in mountains which belong to the youngest of the fold-mountain systems of the earth. The mercury occurs along these mountains in rocks of all ages; but it is restricted to great fractures and overthrusts made by the compression of the earth's crust during the formation of the fold-mountains, as is well shown at Idria. The mercury-fields occur along the Kainozoic fold-mountain system, which includes the Alps, the Himalaya, and the mountains of Western America, at places where the proximity of older dislocations or the branching of the younger mountain lines has led to movements of especial complexity.

With the exception of mercury the Alpine mountains are poor in ores, except when they happen to include rocks charged with metals before the Alpine movements. Analogy, however, with the fold-mountains of the Hercynian system, which preceded the Alpine, suggests that the roots of the later fold-mountains may contain large supplies of ore. The wrecked fragments of the older mountains yield little mercury, as the upper zone that may have contained it has been swept away. The roots of the older mountains are now exposed, and are often rich in ores of the base and precious metals. For example, the fragments of the Hercynian

mountain system contain the copper and tin ores of the south-west of England, the lead ores of the Pennines and the Peak, the copper ores of southern Spain, and most of the ores of Central Europe; the ore deposits along the Appalachians in America occur along earth-movements of the same date.

The different geographical distribution of ores which date from different periods is illustrated by the contrast between that of ores of mercury and of the equally sporadic ores of tin. The main supplies of tin come from the region around the Malay Peninsula, including South Burmah and the islands of Banka and Billiton north of Java; also from Bolivia, Cornwall, Nigeria, and Tasmania. In the last pre-war year (1913), the output was as follows:

	Metric tons.
Malaysia and adjacent areas	87,376
Bolivia	26,327
Australia	7,780
United Kingdom	5,288
Nigeria	3,872
South Africa	2,521

The geological distribution of the tin-fields has clearly no connexion with the Kainozoic fold-mountain system. The historic tin-fields of Europe (Cornwall and the Zinnwald of Germany) are not related to the Alps, but to the Hercynian mountains, which were formed at the end of the Carboniferous Period. Similarly, in Asia, the tin-fields are not along the Himalayan but along the Indo-Malayan mountains, which correspond in age with the Hercynian mountains of Europe. In South America, the Bolivian tin-field lies on the ancient plateau to the east of the Kainozoic fold-lines of the Andes, and the two chief fields of Africa (Nigeria and the Transvaal) are also in areas remote from recent fold-mountains.

The tin-fields occur where granites were intruded at the end of the Palæozoic Period. The tin was not deposited in the heart of the granite masses, but at their upper surface. This fact explains why in South Burmah, for example, the tin is richest beside small outcrops of granite, and sparse beside the larger granite masses; the large outcrops belong to masses of which the tin-impregnated surface has been swept away, whilst the small outcrops are the tips of projections from the granite intrusions and therefore retain the upper surface.

In a district where the granite is so young that none of it is exposed at the surface, any tin ores that may have been formed will be completely buried. On the other hand, the oldest granites do not contain tin in commercial quantity, sometimes because their upper surfaces have been swept away by denudation and sometimes

because the granite was formed at depths where the temperature was too high for tin deposition. Hence, whilst mercury is characteristic of the fractured zone on the crest of the younger fold-mountains, tin is characteristic of the granitic intrusions of the preceding episode of fold-mountain formation. The tin-bearing mountains are sufficiently old for their foundations to be exposed, but they are not so old that the tin-bearing zone has been removed by denudation.

In the case of other base metals, the relations of distribution and age are more complex. Many mining fields have been disturbed by successive crustal movements and have received more than one charge of ores; for example, the Erzgebirge of Saxony received one set of ores during the Hercynian movements and a further series during the Alpine movements.

Earlier in age than the base metals, and characteristic of a still deeper zone of the crust, are the archæan blocks which contain the chief goldfields of West Australia, India, Brazil, South Africa, and parts of the United States.

The mercury and gold-quartz lodes are therefore at opposite ends of the lode series. The ores of the base metals extend the principle that ore deposits depend on depth of formation to intermediate depths. It has often been pointed out that different ores are characteristic of different temperatures and depths; thus tin lodes pass up to copper (Cornwall). Copper may give place upward to lead and silver, or zinc, as in North Queensland; tin may either precede or succeed tungsten, according to local conditions. If temperature were the main factor determining lode formation, then one vein might be expected to pass upward through the whole succession of metals from gold, through tin, tungsten, copper, silver, lead, and zinc to mercury. The nature of the ore supply at any place must depend, however, mainly on the composition of the deeper parts of the crust. Where lodes are fed from basic material, copper, lead, and nickel are more likely to be found than tin and tungsten, which are characteristic of acid rocks, or gold, which is the characteristic metal associated with sub-acid rocks such as grano-diorites. The temperature factor in distribution is overridden by the chemical constitution of the underlying magma.

The localised occurrence of ore formations is explained by their occurrence above elevations of the barysphere and where the main folds are traversed by cross fractures. These positions must be irregularly distributed in accordance with the irregular undulations of the barysphere; but its variations in composition are doubtless within similar limits all the world over. Therefore, although ore deposits are sporadic and large areas are ore-less, the ordinary ores

are scattered widespread over the earth. The distribution of even that deplorably scarce metal, platinum, is world-wide. All the continents have some occurrences, although not necessarily in commercial quantities, of most metals; but the quantities accessible in any area vary with its geological history and stage of denudation. Continents with especially large outcrops of old rocks, such as Australia, Africa, and the Indian Peninsula, owing to the great antiquity of their land surface, expose primary gold ores and are barren in mercury; such areas are often rich in efflorescent ores and products such as manganese, laterite, and bauxite.

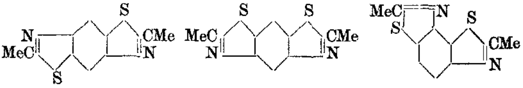
The distribution of the metalliferous lodes is not explained by magmatic segregation in the crust, but by local uprisings of the barysphere in association with the fold-mountain belts; the distribution of lodes is dependent on the major compression belts, which have occupied different positions in the successive disturbances which have deformed the crust of the earth at intervals throughout geological time.

LXXXIV.—*Benzbisthiazoles.*

By Stephen Rathbone Holden Edge.

Some previous experiments with derivatives of benzothiazoles suggested the desirability of investigating the benzbisthiazoles. The only representative of this class of compound hitherto encountered is that described under the name of diethenyl-2 : 5-disulphydro-*p*-aminobenzene, which was obtained by Green and Perkin (T., 1903, **83**, 1204) from *p*-phenylenediaminedithiosulphonic acid and acetic anhydride.

This bisthiazole, from its method of preparation, undoubtedly has the formula (I), and is systematically named 2 : 6-dimethyl-β-benzbisthiazole. For the present experiments *m*-phenylene-



(I.) (II.) (III.)

diamine was taken as the starting point, and from it, by means of the thioacetyl compound, 2 : 6-dimethylbenzbisthiazole (II) or 2 : 7-dimethylbenz*iso*bisthiazole (III) was obtained. The method employed was to convert acetylated *m*-phenylenediamine into

the corresponding dithioacetyl compound, $C_6H_4(N{:}CMe{\cdot}SH)_2$, and oxidise this in alkaline solution with potassium ferricyanide.

Evidence of the existence of a monothiodiacetyl compound, $COMe{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}CMe{\cdot}SH$, was obtained, and this forms an interesting mixture of constant composition with the dithioacetyl compound in the ratio of seven molecules of the dithio- to two molecules of the monothio-compound. This mixture has a sharp melting point and can only with difficulty be resolved into its components.*

Both these benzthiazoles (I and II) have a well-marked basic character; they are soluble in all ordinary acids and quite insoluble in water or alkalis. Their salts are extraordinarily soluble in water and difficult to crystallise. In melting point, crystalline form, and general appearance they are closely alike. Because of this similarity, II is regarded as being the more probable of the two possible formulæ for the new bisthiazole. Further work is being done to determine this point. There is one striking difference between the two. The new bisthiazole (II) is only a monoacid base. It forms only a monohydrochloride even with concentrated acid, and a monomethiodide with a large excess of methyl iodide. The β-benzbisthiazole (I), on the other hand, readily forms a dimethiodide.

In view of the difference between the two bisthiazoles (I and II) noted above, it is of interest that in the phenanthroline series, although these compounds appear to possess only the unsymmetrical structure, phenanthroline itself, having the nitrogen atoms in the meta-position, forms only a monomethiodide, and its diacid salts are unstable in presence of water, whilst ψ-phenanthroline, having the nitrogen atoms in the para-position, readily forms a dimethiodide and stable diacid salts (Skramp and Vortmann, *Monatsh.*, 1882, **3**, 571; 1883, **4**, 574). The same relation seems to hold with the methylphenanthrolines investigated by Gerderssen (*Ber.*, 1889, **22**, 246, 249, 253) and by Willgerodt and Jablonski (*ibid.*, 1900, **33**, 2927). This point is also receiving careful attention in work now being done.

No way could be found of preparing thioacetyl-*p*-phenylenediamine, so that the method of Green and Perkin had to be used in order to prepare the 2 : 6-dimethyl-β-benzbisthiazole.

EXPERIMENTAL.

*Mixture of Mono- and Di-thioacetyl-*m*-phenylenediamines.*—An intimate mixture of 50 grams of diacetyl-*m*-phenylenediamine

* A somewhat similar case is described by Ungar and Hofmann (*Ber.*, 1896, **29**, 1364).

and 25 grams of finely powdered phosphorus pentasulphide is boiled under reflux with 500 c.c. of dry toluene for one hour. When cold, the dark-coloured solid, having been freed from toluene by filtration and evaporation, is treated with excess of 20 per cent. sodium hydroxide; after agitation and keeping for some time, the solution of the sodium derivatives of the thioacetyl-*m*-phenylenediamines is diluted and filtered from unchanged diacetyl-*m*-phenylenediamine. On acidifying the solution with concentrated hydrochloric acid, the thioacetyl derivatives are thrown out as a dark-coloured, finely divided solid. This product, when dried, although containing about 25 per cent. of the monothiodiacetyl derivative, gives satisfactory results on oxidation to the bisthiazole.

Crystallisation from alcohol, with the use of animal charcoal, yields a yellowish-white powder of minute, needle-shaped crystals melting at 181·5°. The melting point is raised by admixture with an equal quantity of either the dithio- or the monothiodiacetyl-*m*-phenylenediamine. Slight contamination with either constituent has practically no effect on the melting point except to make it less sharp. The sharp melting point and the constancy of composition of this product would indicate that it is a eutectic mixture (Found: C = 54·51; H = 5·37; S = 25·83. Calc. for 3 mols. of the dithio- to 1 mol. of the monothio-derivative: C = 54·55; H = 5·45; S = 25·46. Calc. for 4 mols. of the dithio- to 1 mol. of the monothio-derivative: C = 54·37; H = 5·43; S = 26·09 per cent.).

Dithioacetyl-m-*phenylenediamine.*—After four crystallisations from 200 c.c. of alcohol, the mixture (25 grams) obtained above yielded 4·5 grams of slender, yellow crystals melting at 194°. Further recrystallisation produced no effect on the melting point (Found: S = 28·24. Calc., S = 28·58 per cent.).

Monothiodiacetyl-m-*phenylenediamine.*—The mother-liquor from the first crystallisation above was concentrated to 50 c.c. and poured into a litre of water, whereby the main bulk of the double compound was precipitated. This was filtered off and the water solution concentrated. In this way 3 grams of a solid melting above 196° were obtained, and after three further crystallisations the m. p. was 220°. Shortage of material prevented further purification (Found: S = 18·52. Calc., S = 15·38 per cent.).

2 : 6-*Dimethylbenzbisthiazole* (*II*) *or* 2 : 7-*Dimethylbenzisobisthiazole* (*III*).—A solution of 20 grams of crude dithioacetyl-*m*-phenylenediamine and 67·5 grams of sodium hydroxide in 1000 c.c. of water is added to 133·5 grams of potassium ferricyanide dissolved in 1400 c.c. of water. The feathery precipitate that forms is collected

after three days and extracted with ether, the ethereal solution is dried and evaporated, and the residue is distilled, preferably under reduced pressure, whereby 6·5 grams of an oil, solidifying to a hard, yellow solid on cooling, are obtained. Recrystallisation from hot light petroleum gives beautiful, very pale yellow crystals, m. p. 106°, b. p. 342—344° or 240°/45 mm. (Found : C = 54·46; H = 3·57; S = 28·71. $C_{10}H_8N_2S_2$ requires C = 54·55; H = 3·63; S = 29·02 per cent.).

The *hydrochloride*, prepared in concentrated acid solution, forms colourless, stout crystals, m. p. 215° (Found: Cl = 13·82. $C_{10}H_8N_2S_2,HCl$ requires Cl = 13·84 per cent.).

The *methiodide*, prepared by heating the bisthiazole with excess of methyl iodide in a sealed tube in a water-bath for two days and purified by crystallisation from either alcohol or water, forms nearly colourless crystals, which darken on heating and melt with decomposition at 236°. For some unexplained reason, the iodine content of this compound is about 1 per cent. too high. Repeated crystallisation and strong heating even at 180° for some hours (at which temperature some decomposition takes place) produce no appreciable effect. Four analyses on different samples gave I = 36·14, 35·96, 35·99, 36·25 ($C_{10}H_8N_2S_2$,MeI requires I = 35·09 per cent.).

No evidence of the existence of a dimethiodide could be obtained. After long heating with a large excess of methyl iodide, the resulting solid, air-dried, showed barely the increase of weight required by the monomethiodide and on crystallisation gave a compound identical with that described above.

2 : 6-*Dimethyl-β-benzbisthiazole Dimethiodide.*—The bisthiazole (I), prepared as described by Green and Perkin (*loc. cit.*), ten times the quantities given being employed, is heated with excess of methyl iodide in a sealed tube in a water-bath for a few hours. The product, crystallised from water, dried thoroughly at 150°, and cooled in a vacuum desiccator, is a yellow, crystalline powder, which darkens on heating and melts with decomposition at 238° (Found : I = 50·38. $C_{10}H_8N_2S_2$,2MeI requires I = 50·4 per cent.).

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LXXXV.—*Heterogeneous Equilibria: The Ternary System Sodium Sulphate–Sodium Carbonate–Water.*

By Alfred Ernest Dawkins.

The following research was undertaken as a contribution to the knowledge of the solubility relations, hitherto unrecorded, of the two simple salts, sodium sulphate and sodium carbonate, a matter of importance in the heavy chemical industry.

The isothermal relationships have been investigated at two temperatures, namely, 19·1° and 50°, the former being chosen as representing about the lowest temperature that can be conveniently maintained in an ordinary laboratory during the winter. Complete data have been obtained for the isotherm at 19·1°. The data at the higher temperature, 50°, are incomplete, but are sufficient to indicate the general nature of the equilibrium relationships.

At both temperatures a preliminary exploration was carried out by means of Schreinemakers's well-known "residues method." Owing, however, to the formation of solid solutions at both temperatures, this method was not sufficient to fix the composition of the solid phases with certainty. Supplementary experiments for the isolation and analysis of the solid phases were carried out at the lower temperature, but at the higher temperature it was not found possible in the time available to proceed beyond the preliminary Schreinemakers exploration.

Experimental.

The chemicals used were Messrs. Hopkin and Williams's "guaranteed reagents." The thermostat in which the components were brought to equilibrium was provided with a gas temperature-regulator of the ordinary type. The apparatus in which the saturated solutions were prepared and the corresponding wet solids obtained for examination by Schreinemakers's method, consisted of a wide glass test-tube provided with a rubber stopper carrying (*a*) a stirrer, and (*b*) a narrow glass tube, over the end of which was secured a piece of finely woven cloth, serving as a filter. The narrow glass tube was capable of being slid up and down through the stopper, and was kept clear of the mixture in the test-tube until it was desired to separate the phases for analysis, when it could be pushed down through the mass of liquid and crystals to the bottom of the test-tube. The liquid for analysis was sucked off into a smaller test-tube provided with a two-holed stopper, one hole carrying a tube in connexion with the filtering tube, and the other a tube for suction. The tube containing the salts and water was immersed almost com-

pletely in the water of the thermostat, so that the temperature at the lower end of the glass tube for filtering off the solution could not differ sufficiently from that of the thermostat to disturb the equilibrium when the tube was depressed into the mixture below.

For the supplementary examination of solid phases (at 19·1° only), the method described by Fock (*Z. Kryst. Min.*, 1897, **28**, 347) was used; that is, solutions were allowed to evaporate at the temperature of the thermostat until a small crop of crystals appeared. The crystals were picked out of the solution, rapidly pressed between filter-paper, washed twice with an almost saturated solution of sodium sulphate or sodium carbonate as the case might be, then once with water, and finally dried rapidly on filter-paper.

Sodium sulphate was estimated gravimetrically after conversion into barium sulphate, and sodium carbonate volumetrically by titration with standard solutions of hydrochloric acid, using methyl-orange as indicator. The third component, water, was arrived at by difference. All estimations were made in duplicate where possible.

Results.

The Isotherm at 19·1°.—The compositions of the solutions and wet solids obtained by Schreinemakers's method are contained in the following table.

TABLE I.

		Liquid.		Corresponding residue.	
		Grams per 100 grams of liquid.		Grams per 100 grams of residue.	
No. of determination.	Density.	Na_2SO_4.	Na_2CO_3.	Na_2SO_4.	Na_2CO_3.
6	1·19	4·97	15·97	2·34	28·29
1	1·22	9·05	14·92	3·19	30·82
4	1·23	9·50	14·82	4·80	26·88
9	1·29	10·47	14·53	16·88	19·31
8	1·28	10·69	13·84	29·42	6·84
2	1·26	11·06	12·13	28·04	6·37
5	1·21	11·89	9·22	29·30	4·54
7	1·15	13·17	4·85	31·87	2·30

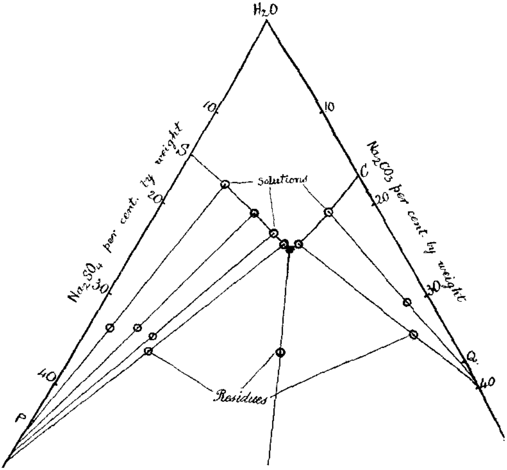
In Fig. 1 these results are plotted graphically on the triangular co-ordinate system.

The points *S* and *C* representing solubilities of sodium sulphate and sodium carbonate in water at 19·1°, are calculated from data given in Seidell's Dictionary of Solubilities.

There are seen to be two *liquidus* curves, intersecting sharply at an invariant point, which must be determined by the presence of two solid phases. But as to the composition of these two solid phases, the diagram does not give definite evidence. In the binary systems Na_2SO_4–H_2O and Na_2CO_3–H_2O the stable solid phases at

19·1° are in each case the decahydrate, represented on the diagram by *P* and *Q* respectively. But that these two decahydrates are not the actual solid phases in equilibrium with the invariant solution is shown by the divergence of the conjugation lines on both sides of the diagram from *P* and *Q*. Similarly, the failure of the conjugation lines to intersect at a definite point inside the diagram indicates that the two univariant systems represented by the two branches of the *liquidus* are determined by the presence, not of a pair of solids

FIG. I.



$P = Na_2SO_4,10H_2O$. $Q = Na_2CO_3,10H_2O$.

of constant compositions, but rather of two series of solid solutions. This indication was confirmed by the isolation and analysis of the actual solid phases in equilibrium with the several solutions (Fock's method, see above). The crystals thus obtained invariably contained both sodium sulphate and sodium carbonate, and a proportion of water agreeing closely with that required for mixtures of the decahydrates. The solid phases thus consist of two series of solid solutions, containing in each case ten molecules of water of

crystallisation. The liquids in equilibrium with each set of crystals were also analysed for one component, which in conjunction with the already determined solubility relations is sufficient to fix the composition of each solution. The compositions of the solid phases obtained in this way and of the corresponding liquids are contained in the following table :—

TABLE II.

Solids Rich in Sodium Sulphate.

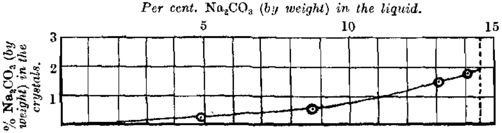
Na_2CO_3 in the liquid—% by weight	4·91	8·72	13·07	14·07
Na_2CO_3 in the solid (decahydrate)—% by weight	0·34	0·60	1·54	1·80

Solids Rich in Sodium Carbonate.

Na_2SO_4 in the liquid—% by weight	3·71	5·57	6·91	7·31	8·97
Na_2SO_4 in the solid (decahydrate)—% by weight	0·74	0·75	0·92	1·13	1·42

In order to fix definitely the shape of the isotherm, it is obviously necessary to determine the composition of the limiting solid solutions

FIG. 2.



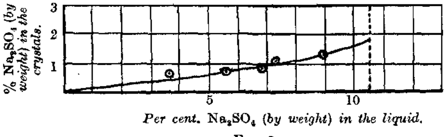
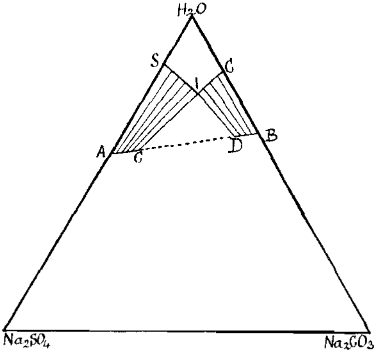


FIG. 3.

which are in mutual equilibrium in the presence of the invariant solution. It has not been found practicable to effect a separation of these two coexisting solid solutions, but a close approximation to their composition can be made by plotting the figures given in Table II and extrapolating for the limiting concentrations of sodium sulphate and sodium carbonate at the invariant point. The graphs are shown in Figs. 2 and 3. The limiting solid solutions are seen to contain 2·00 per cent. of sodium carbonate and 1·90 per cent. of

sodium sulphate respectively. The shape of the complete isotherm is shown in Fig. 4. The points *S*, *I*, *C*, *A*, and *B* are to scale (weight percentages), but the lengths of *AC* and *BD* are exaggerated for the sake of clearness.

Fig. 4.



The Isotherm at 50°.—The analysis of eight pairs of solutions and corresponding wet solids gave the following results:—

No of. determination.	Liquid. Grams per 100 grams of liquid.		Corresponding residue. Grams per 100 grams of residue.	
	Na_2SO_4.	Na_2CO_3.	Na_2SO_4.	Na_2CO_3.
57	5·35	28·66	3·35	66·20
55	5·87	28·52	11·77	52·91
52	7·52	25·71	36·86	26·87
53	12·92	19·37	45·36	22·10
51	20·38	12·55	47·06	16·69
58	22·47	10·52	63·05	11·53
54	23·10	10·21	61·86	6·33
56	27·31	5·06	80·58	1·56

These results are plotted graphically in Fig. 5.

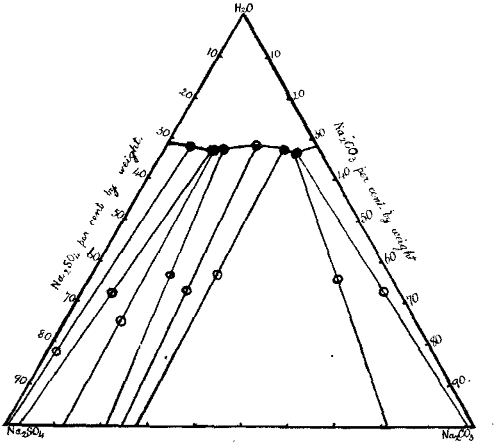
The *liquidus* curve is seen to consist of three portions, intersecting n two invariant points, the compositions of the invariant solutions eing given by determinations 54 and 55 respectively. The irections of the conjugation lines indicate that to each portion of he *liquidus* there corresponds a set of solid solutions. Further ork is required to determine the compositions of these three sets f solid solutions.

Summary.

1. In the ternary system Na_2SO_4–Na_2CO_3–H_2O, the isothermal equilibria at 19·1° and 50° have been investigated.

2. The isothermal diagram at 19·1° consists of a double-branched *liquidus* curve, an invariant point, and two *solidus* curves representing solid solutions in equilibrium with the solutions represented by the two branches of the *liquidus*.

FIG. 5.



3. The isothermal diagram at 50° consists of a triple-branched *liquidus* curve, two invariant points, and three *solidus* curves representing solid solutions in equilibrium with the solutions represented by the three branches of the *liquidus*.

The thanks of the author are due to Professor Donnan, F.R.S., for helpful advice throughout the work, and to Mr. W. E. Garner for several valuable suggestions. The author also makes acknowledgment to the Royal Commissioners of the 1851 Exhibition for the grant of a scholarship.

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LXXXVI.—*Phototropy of Inorganic Salts. Cuprous Chloride and Bromide.*

By GOPAL SINGH.

WHOLER (*Annalen*, 1864, **130**, 273) states that crystals of cuprous chloride, when kept under acidified water and exposed to direct sunlight for five minutes, become dark "copper-coloured" and assume metallic lustre. He explains the change of colour by supposing that an oxychloride is formed, with the simultaneous production of hydrochloric acid.

In the course of some experiments it was observed that when cuprous chloride was exposed to direct sunlight under water slightly acidified with sulphurous acid, it became first greyish-blue, then dark blue, and finally dark "copper-coloured," and assumed metallic lustre after a few minutes' exposure. Further, it was noticed that when this exposed cuprous chloride was kept in the dark, the reverse changes of colour took place—first it lost its metallic lustre, then the dark blue colour changed to greyish-blue, and finally it regained its original white colour in about forty-eight hours. This cycle of changes could be repeated any number of times without loss in the photo-reactive sensitivity of the sample used. The only precaution taken was to protect the cuprous chloride from oxidation by keeping it under acidified water (pure water decomposes cuprous chloride). In other words, cuprous chloride in the presence of water was found to exhibit the remarkable photochemical phenomenon named phototropy.

Cuprous bromide also exhibited phototropy in the same manner. It became dark green after a few minutes' exposure, but the dark "copper colour" did not appear until after an exposure of about half an hour, and even then only very faintly. The reverse changes took place in about thirty hours if the salt had been exposed for a few minutes only.

It may be mentioned that cuprous chloride and bromide are the only inorganic compounds that exhibit phototropy in all samples, whether they are prepared from chemically pure materials or from commercial ones—unlike calcium sulphide (Mourelo, *Compt. rend.*, 1914, **158**, 122).

Cuprous iodide is not phototropic. Cuprous fluoride is still under investigation.

Quite dry cuprous chloride and bromide are not sensitive to light, and even several hours' exposure to bright sunlight produces no change of colour. It is significant that in the presence of completely dry liquids other than water these compounds are not

sensitive to light. Moreover, if the wet, exposed compounds be dried in a vacuum or warmed in an atmosphere of hydrogen, they will regain their white colour as soon as all the moisture shall have been driven off, that is, the coloured modifications of the compounds are only stable in the presence of water.

The time required for the transformation of white cuprous chloride or bromide into the coloured variety varies with the intensity of light, the greater the intensity the quicker the change. Bright sunlight produces appreciable change after a few seconds; arc light takes about a minute, whilst the light of the mercury lamp or of burning magnesium brings about the change after about five minutes' exposure. Even diffused light can act, but in this case the time required to produce appreciable change may be some hours or even days. Electric light or the light of the sodium flame has no action on either of the white substances.

After exposure of the salts to the light of an arc lamp, no phosphorescence was observed on the sudden removal of the source of light. Rubbing of cuprous chloride or bromide between glass plates in the dark-room gave no indication of triboluminescence. Old samples retain their photo-reactive sensitivity unimpaired. Examination under the microscope of exposed crystals showed that the crystalline shape was unaltered. Powdered crystals also exhibited phototropy. Almost all the known solvents for cuprous chloride, namely, ammonium hydroxide, pyridine, quinoline, concentrated hydrochloric acid, and concentrated solutions of alkali haloids, were examined, and in no case was phototropy observed in the solution.

To study the action of light of different colours on cuprous chloride, a long glass tube with a narrow bore was filled with the substance and a little sulphurous acid and then sealed and exposed to the light of the spectrum. After an exposure of about five minutes, that part of the salt which had been exposed to the violet portion of the spectrum developed a dark blue colour, and after further exposure the remaining parts also developed colour. It was observed that the maximum effect was produced by violet light, and the least by red. Cuprous bromide behaved exactly in the same manner as cuprous chloride, it also being most sensitive to violet light.

At the ordinary temperature the effect of exposure of cuprous chloride or bromide to direct sunlight is rapid, but the reverse action in the dark is very slow. Cuprous chloride at about 20° is covered with dark copper-coloured crystals after five minutes' exposure, but decoloration at that temperature requires about forty-eight hours. At higher temperatures, whilst the velocity of

coloration decreases very slowly, the velocity of decoloration increases rapidly. Thus decoloration of cuprous chloride at 100° takes about half an hour, whilst at 200° the substance recovers its original white colour in a few minutes.

It is noteworthy that the sensitiveness to light of cuprous chloride and bromide is affected by the presence of acids. The sensitiveness decreases with the increase in concentration of the acid. In the following table is given the concentration of acid which altogether inhibits the action of light on the substances.

	Grams of acid per c.c.			
Substance	H_2SO_4.	HCl.	$CH_3 \cdot CO_2H$.	H_2SO_3.
CuCl	1·172	0·221	1·024	sensitive in all *concentrations*
CuBr	0·870	0·044	0·768	,,

It will be seen from the above table that the sensitiveness of cuprous bromide is more affected by the presence of acids than that of cuprous chloride, and further that hydrochloric acid exerts the greatest inhibiting effect.

As regards the mechanism of the change, it may be stated at the outset that atmospheric oxygen takes no part, for in all the experiments the cuprous chloride and bromide were protected from it by keeping them under acidified water. Wholer's explanation (*loc. cit.*), which is based on the supposition that water acts on cuprous chloride in the presence of sunlight, producing an oxychloride with the simultaneous formation of hydrochloric acid, does not seem to be correct: First, because hydrochloric acid could not be detected even after many hours' exposure; secondly, because the coloured modification, as has been shown, changes back to the original substance when it is kept in the dark. If Wholer's explanation be applied to the reverse reaction, it would mean that hydrochloric acid and the oxychloride again react with each other in the dark to reproduce the original substance and water. This reverse reaction is only possible in the presence of hydrochloric acid. But experiments have shown that if the exposed substance be thoroughly washed with alcohol in order to remove the hydrochloric acid which Wholer supposes is produced in the direct reaction, and be then kept in the dark, it will still revert to the original substance. Unlike the complex phototropic organic compounds such as the fulgides of Stobbe (*Annalen*, 1908, **359**, 1), the molecule of cuprous chloride or bromide is a very simple one, and therefore dynamic isomerism is excluded. The one apparent explanation which can be put forward is that the substance combines with water in the presence of light to form some kind of hydrate and that this hydrate is not

stable in the dark, and therefore breaks up again into water and the original substance when it is kept in the dark. But it may be stated that there is no experimental evidence to support this explanation, and at present one cannot definitely say what part water plays in the reaction.

Experiments are being continued to find a quantitative relation between temperature and phototropy which might throw some light on the mechanism of the change.

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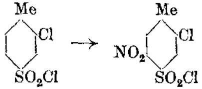
LXXXVII.—*The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. Part III.*

By WILLIAM DAVIES.

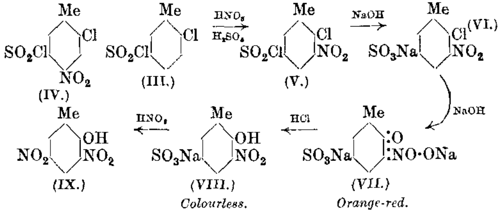
THE nitration of 2-chloro-*p*-toluenesulphonyl chloride (Davies, T., 1921, **119**, 859) apparently shows that the chlorine atom has far greater directing power than the other two substituents acting together.



An explanation of many unexpected substitutions in poly-substituted benzene derivatives such as those described by Simonsen and Rau (T., 1917, **111**, 221, 222) is due to Professor Robinson (Perkin and Robinson, T., 1914, **105**, 2379; Jones and Robinson, T., 1917, **111**, 906), who found in many cases that when a negative group is in the ortho- or para-position to a positive group, it neutralises such a group, and the orientating effect is exercised by the second positive group. (This statement is attributed to Robinson by Gibson, Simonsen, and Rau, T., 1917, **111**, 73). The nitration of (I) is in accordance with this rule.

In order to determine whether the large amount of (II) is actually attributable to this supposed neutralisation of the negative and positive centres in the para-position to each other in (I), the nitration of 6-chloro-*m*-toluenesulphonyl chloride (III) was carried out under comparable conditions. If the directive influences of the chlorine

atom and the sulphonyl chloride group neutralise each other,* then (IV) *ought to be the chief product; if not,* (V) *might be expected to* predominate.



The nitration of (III) leads to the formation of a 90 per cent. yield of (V), and although a small quantity of oil is formed, no other isomeride can be isolated. This experiment serves to show that Robinson's rule is not valid in this case,† and that, as might be expected, the ortho-directing power of the chlorine atom together with the meta-directing influence of the sulphonyl chloride group *overwhelms the effect of the methyl group. It follows that the* explanation of the formation of (II) in such large amount is to be found in the great para-directing power of the chlorine atom.

The constitution of the chloronitrotoluenesulphonyl chloride produced in the nitration of (III) is shown by replacing with hydroxyl the chlorine atom in the corresponding sodium sulphonate (VI), by the action of boiling sodium hydroxide solution. The substance formed shows all the properties that would be expected from a

* It is perhaps scarcely legitimate to imagine this kind of "neutralisation" occurring between two such "acigenic" or "acylous" substituents as –Cl and $-SO_2Cl$; but it must be remembered that –Cl (ortho-para-directing) *resembles in many ways a so-called "positive" group like –OH, and that* such "neutralisation" between –OH and $-SO_2Cl$ is quite admissible. For example, chloroacetic acid and glycollic acid are both stronger than acetic acid (Kauffmann, "Beziehungen zwischen Physikalischen Eigenschaften und Chemischer Konstitution," 1920, pp. 346, 349), despite the fact that one substituent is called "positive" and the other "negative." A valuable attempt to introduce order into the use of the terms "positive" and "negative" has recently been made by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii. 1).

† It should be mentioned that Robinson himself (*loc. cit.*) seems to apply his rule only to aromatic substances in which the two so-called "positive" (ortho-para-directing) groups are either identical or very similar. This research shows, at any rate, that the rule cannot always be applied when the two ortho-para-directing groups are dissimilar.

sodium salt of a nitrocresolsulphonic acid. The neutral and acid salts differ markedly in colour, as would be anticipated from the formulæ VII and VIII.

These salts are converted by the action of hot dilute nitric acid *into 3 : 5-dinitro-o-cresol* (IX) *and sulphuric acid*. Moreover, a phenolic substance and sulphuric acid are produced by treating (VIII) with hydrobromic acid and bromine water.

An extremely interesting difference in solubility exists between the sodium and potassium salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid. The sodium salt is readily soluble and the potassium salt very sparingly soluble in cold water. A *N*/50-solution of potassium chloride deposits the potassium sulphonate on the addition of a solution of the sodium sulphonate. Both salts contain no water of crystallisation, and may be of value for the estimation of potassium in the presence of sodium salts, for the perchlorate method recently elaborated for the estimation of potassium (*Annual Reports*, 1920, **17**, 148) is apparently troublesome.

EXPERIMENTAL.

*6-Chloro-*m*-toluenesulphonyl Chloride*.—*o*-Toluidine-5-sulphonic acid was prepared by heating *o*-toluidine (1 part) with 3 parts of sulphuric acid containing a trace of iodine for six hours at 160—165°; the amount of charring at this temperature was negligible. The weight of the once crystallised sulphonic acid (from water) was the same as that of the *o*-toluidine taken. This sulphonic acid was converted into sodium 6-chloro-*m*-toluenesulphonate in the following way, advantage being taken of the sparing solubility of the sodium salt in concentrated hydrochloric acid: *o*-Toluidine-5-sulphonic acid (150 grams), suspended in a mixture of concentrated hydrochloric acid (450 c.c.) and powdered ice (300 grams) in a freezing mixture, was diazotised with a concentrated solution of sodium nitrite (75 grams of 95 per cent.); a large amount of diazonium compound separated towards the end of the reaction. The mass was carefully added to a cold solution of cuprous chloride (110 grams) in concentrated hydrochloric acid (800 c.c.) and water (150 c.c.), the product heated on the water-bath for one and a half hours, when the copper diazonium derivative was completely decomposed, and the green solution allowed to remain over-night. The deposit of colourless leaflets was collected, washed with a little water, and dried at 160°. The yield (99 grams) can be considerably increased by re-concentrating the diluted filtrate after removal of the copper as sulphide.

Sodium 6-chloro-*m*-toluenesulphonate (100 grams) was converted into the corresponding sulphonyl chloride (95 grams) melting at

64—66° by means of phosphorus pentachloride in the usual way. The melting point recorded by Wynne (T., 1892, **61**, 1040) is 65°.

*Nitration of 6-Chloro-*m*-toluenesulphonyl Chloride.*—The chloride (100 grams) was added to a mixture of nitric acid (75 c.c.; *d* 1·50) and sulphuric acid (150 c.c.) at 26°, and the mixture stirred. The temperature fell to 25° and then slowly rose to 35°, when the nitration mixture was cooled and the nitration carried out between 28° and 35°. The reaction was finished in ninety minutes. The product was poured into a large volume of ice-water, and the nitro-derivative well washed with water, when it rapidly solidified to a hard, brittle mass. This substance, when dried under diminished pressure over phosphoric oxide, melted at 41—46° and weighed 112 grams.

Attempted Separation of the Isomerides.—The nitration product was crystallised from light petroleum (b. p. 80—100°) and after repeated crystallisation 85 grams of one isomeride melting at 47—50° were obtained in long, thick, colourless rods. The last-crystallising fractions contained several small rhombohedral crystals melting at 85—88°, but there was insufficient of this isomeride for analysis. However, the portion of the nitration product least soluble in light petroleum only partly solidified on long standing, and weighed 19·8 grams. Advantage was taken of the sparing solubility of potassium 6-chloro-5-nitro-*m*-toluenesulphonate to separate the corresponding sulphonyl chloride from the oily mixture in the following way. The mixture was boiled with alcohol (75 c.c. of 94 per cent.) for two hours and the alcohol distilled off. The residue dissolved completely in water, and the solution, neutralised with sodium hydroxide and diluted to 300 c.c., was mixed with a solution of potassium chloride (6 grams) in 50 c.c. of water, when almost pure potassium 6-chloro-5-nitro-*m*-toluenesulphonate was instantly precipitated; collected after remaining over-night, and dried at 150°, it weighed 16·7 grams. The filtrate was evaporated to dryness and, after heating for two hours at 150°, the mixture of salts weighed 9·6 grams. The mixture was heated with 10 grams of phosphorus pentachloride for an hour on the water-bath and the cold product poured into cold water, when an oil (4 grams) was obtained. As the oil refused to solidify, and no pure sulphonamide could be derived from it, the investigation of this small proportion of isomerides was abandoned. The weight of the potassium salt (16·7 grams) corresponded with 15·6 grams of 6-chloro-5-nitro-*m*-toluenesulphonyl chloride, so that the total yield of this substance is about 100·6 grams, or 90 per cent. of the nitration product.

*6-Chloro-5-nitro-*m*-toluenesulphonyl chloride* (V) is moderately soluble in boiling light petroleum and slightly soluble in the cold

solvent, from which it crystallises in long, colourless prisms melting at 49—50° (Found : N = 5·1. $C_7H_5O_4NCl_2S$ requires N = 5·2 per cent.). When it is boiled with alcoholic alkali or hydrazine hydrate, characteristic colorations are produced, which are due to the reactivity of the chlorine in the nucleus.

The *amide*, made by boiling the sulphonyl chloride with dilute ammonia solution, is moderately soluble in boiling, and sparingly soluble in cold, water. It dissolves readily in hot alcohol, slightly in cold, from which it crystallises in small, colourless needles melting at 201—202° (Found : N = 11·1. $C_7H_7O_4N_2ClS$ requires N = 11·2 per cent.).

The *sodium* salt cannot be prepared in the usual way in a pure state, but is conveniently obtained as follows. The sulphonyl chloride (25·6 grams; 1 mol.) is boiled under reflux for five hours with alcohol (50 c.c. of 90 per cent.), and the red solution, which smells of hydrogen chloride, evaporated on the water-bath to small bulk, when the sulphonic acid separates out on cooling in colourless needles. The solution is diluted with water and again concentrated, and this procedure is repeated twice, when the product will be free from hydrochloric acid. The liquid is titrated with sodium hydroxide, 3·9 grams being required (1 mol. of the acid requires 4·0 grams). The solution is evaporated to dryness and the yellow salt crystallised from water, when the pure sodium salt separates in colourless scales containing no water of crystallisation (Found : H_2O = 0·3; Na = 8·8. $C_7H_5O_5NClSNa$ requires Na = 8·4 per cent.).* The sodium salt is readily soluble in cold and extremely soluble in hot water. The difference in solubility between the sodium and potassium salts is extraordinarily great, and by means of the former a rapid and moderately accurate estimation of the potassium in a mixture of sodium and potassium salts can be carried out.

The *potassium salt rapidly separates as colourless, glistening* scales when a solution of the sodium salt is mixed with potassium chloride solution (Found: in air-dried material, H_2O = 0·2; K = 13·8. $C_7H_5O_5NClSK$ requires K = 13·5 per cent.). The salt is sparingly soluble in cold and slightly soluble in boiling water.

The alkali salts of the sulphonic acid on the whole seem to follow the rule of decreasing solubility with increasing atomic weight of the metal, which usually holds for salts derived from strong acids. The *lithium* and sodium salts are readily soluble, the *ammonium* salt (needles) slightly soluble, and the potassium and *rubidium* salts sparingly soluble in cold water. The rubidium salt consists of colourless needles less soluble than rubidium hydrogen tartrate.

* In estimating the metal in the sodium and potassium salts, very careful heating is necessary to avoid sudden deflagration and consequent loss.

The *cæsium* salt (colourless needles) is exceptional, however, for it is almost as soluble as the sodium salt.

The *magnesium* salt is very soluble; the *barium* salt (needles) is slightly soluble in cold and readily soluble in hot water.

Derivatives of 3-*Nitro*-o-*cresol*-5-*sulphonic Acid*.—6-Chloro-5-nitro-*m*-sulphonyl chloride (20 grams) was boiled with excess of sodium hydroxide solution (100 c.c. of 12 per cent.). The liquid rapidly became a clear deep red and after four hours portions of the resulting solution (A) were diluted and treated with the following reagents:—

(1). Potassium chloride solution. No precipitate was obtained, but when the mixture was treated with two drops of a solution of sodium 6-chloro-5-nitro-*m*-toluenesulphonate, the corresponding potassium salt separated at once. Hence the solution (A) contained no appreciable quantity of sodium 6-chloro-5-nitro-*m*-toluenesulphonate.

(2). Hydrobromic acid. The solution became yellow and a white precipitate was formed which dissolved on warming. The solution was free from sulphuric acid. Bromine water was added and the mixture boiled, when a small amount of solid separated and sulphuric acid was produced.

(3). Dilute nitric acid. When the acid solution was cautiously warmed, a reaction took place at 90—95°, a large quantity of a yellow oil separating. Heating at 90—95° for two minutes made the reaction (in which sulphuric acid was produced) almost quantitative. The oil solidified on cooling, and crystallised from alcohol in pale yellow needles melting sharply at 85·5°. This substance dissolved in sodium hydroxide solution with an orange colour and was slightly volatile in steam. These and other properties indicated that the substance was 3 : 5-dinitro-*o*-cresol, and this deduction was confirmed by direct comparison with an authentic specimen (m. p. 85°) and by the method of mixed melting points.

(4). Hydrochloric acid and a concentrated solution of ferric chloride. The solution on boiling became dark and an odour similar to that of *p*-benzoquinone became very perceptible.

These experiments sufficiently justify the constitution assigned to the chloronitrotoluenesulphonyl chloride melting at 49—50°.

Salts of 3-*Nitro*-o-*cresol*-5-*sulphonic Acid*.—The differences in the colour and solubility existing between the neutral and acid salts of 3-nitro-*o*-cresol-5-sulphonic acid cause them to possess some interest.

The undiluted remaining solution (A) (90 c.c.) was cooled and kept over-night, and the sodium salt (about 12 grams) was collected. After recrystallisation from water, the neutral *sodium* salt separated

in thick orange-red prisms, which dissolved readily in hot and less readily in cold water to form a red solution.

The neutral *barium* salt, obtained by double decomposition from the sodium salt, is a scarlet powder sparingly soluble in water, hot or cold. It can also be prepared by mixing a solution of the acid barium salt with baryta water (Found: in anhydrous material, Ba = 36·3. $C_7H_5O_6NSBa$ requires Ba = 37·3 per cent.)

The neutral *lead* salt consists of orange, microscopic crystals sparingly soluble in hot and almost insoluble in cold water.

The acid *sodium* salt separates as minute, colourless crystals when a moderately concentrated solution of the neutral sodium salt is acidified with sulphuric or hydrochloric acid. Its solubility in water is of the same order as that of the neutral salt.

The acid *barium* salt can be obtained either by the action of hydrochloric acid on an aqueous suspension of the neutral salt or by double decomposition from the acid sodium salt. When the second method is used, the barium salt rapidly crystallises in characteristic spherical clusters of colourless needles slightly soluble in cold and readily soluble in boiling water [Found: in anhydrous material, Ba = 21·9. $(C_7H_6O_6NS)_2Ba$ requires Ba = 22·4 per cent.].

The acid *silver* salt forms colourless needles moderately soluble in water.

Summary.

(1). 6-Chloro-*m*-toluenesulphonyl chloride is converted by nitration with mixed nitric and sulphuric acids almost entirely into *6-chloro-5-nitro-m-toluenesulphonyl chloride*. This substance is readily transformed by boiling sodium hydroxide solution into the neutral sodium salt of 3-nitro-*o*-cresol-5-sulphonic acid.

(2). The result of the nitration of 6-chloro-*m*-toluenesulphonyl chloride and of 2-chloro-*p*-toluenesulphonyl chloride (Davies, *loc. cit.*) indicates that the chlorine atom has, as far as nitration is concerned, a much greater directing effect in this type of trisubstituted benzene derivative than is generally supposed.

The author wishes to make acknowledgment to the Ramsay Memorial Fellowship Trust for a Fellowship which has greatly facilitated this research.

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LXXXVIII.—*Pyridinium Salts derived from some Chloroacetylamino-compounds.*

By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

THE preparation of pyridinium salts derived from chloroacetylamino-compounds was undertaken with the view of studying the tinctorial properties of azo-dyes containing this grouping, but it was found that both the chloroacetylamino-compounds themselves and the pyridinium salts derived from them are so easily hydrolysed that dyes containing this group would be valueless.

Pyridinium salts derived from chloroacetylamino-compounds do not seem to have been described previously, and hence it has been considered worth while to publish a short description of some typical compounds of this class.

Chloroacetyl derivatives of the amines have been prepared by several investigators (Meyer, *Ber.*, 1875, **8**, 1153; Eckenroth and Donner, *ibid.*, 1890, **23**, 3287; Stolle, *ibid.*, 1893, **47**, 2120; Wallach, *Annalen*, 1882, **214**, 221; Frerichs, *ibid.*, 1887, **241**, 211; Tommasi, *Bull. Soc. chim.*, 1873, [ii], **19**, 400; **20**, 21; Abenius and Widmann, *J. pr. Chem.*, 1888, [ii], **38**, 299; Deutsch, *ibid.*, 1907, [ii], **76**, 354; Johnson and Cramer, *J. Amer. Chem. Soc.*, 1883, **25**, 485, 491; Kuhara and Chikashige, *Amer. Chem. J.*, 1902, **27**, 6; Clarke, T., 1910, **97**, 429) by the action of chloroacetyl chloride on primary and secondary amines, and those derived from primary amines are remarkable for the irritant effect that they have on the skin. They are much more easily hydrolysed than the corresponding acetyl compounds, hydrolysis being effected in nearly every case by warming with dilute sodium carbonate solution. In this respect, the chloroacetyl derivative of 2-aminoanthraquinone is particularly remarkable, as it is hydrolysed by merely boiling for a few minutes with alcohol, and a sample which had been recrystallised from this solvent was found to contain 20 per cent. of the free primary amine.

The chloroacetyl derivatives of the primary amines, when warmed with a solution of calcium hypochlorite, pass into the carbylamine, and the corresponding pyridinium salts do the same, although no trace of carbylamine can be detected when acetanilide is treated with a hypochlorite. The production of carbylamine and the ease with which the chloroacetylamino-compounds undergo hydrolysis suggested that they might have the azo-methine structure, $ArN{:}C(OH){\cdot}CH_2Cl$, and this receives support from their physiological action, as irritant properties nearly always appear when a halogen atom is conjugated with a double bond or with an element showing residual affinity. Numerous attempts were made to establish the

correctness of the azo-methine structure by the preparation of an *O*-methyl ether by the action of methyl sulphate on ω-chloroacetanilide, but in every case negative results were obtained owing to hydrolysis taking place and to the formation of resinous matter.

Previous investigators have always prepared chloroacetyl compounds by the action of 1 molecule of chloroacetyl chloride on 2 molecules of the amino-compound, anhydrous ether or benzene being used as a solvent, and this method is quite satisfactory when dealing with inexpensive amines and with amines which give easily soluble hydrochlorides. Only half the amine is converted into the chloroacetyl derivative, and in the case of an amine, such as *p*-toluidine, which gives a sparingly soluble hydrochloride the purification of the resulting chloroacetylamino-compound may be troublesome. Much better results have been obtained by carrying out the reaction in the presence of quinoline, as under these conditions the whole of the amine is converted into its chloroacetyl derivative, and as quinoline hydrochloride is very easily soluble in cold water the purification of the product is easy. As a solvent, chloroform is much to be preferred to either ether or benzene owing to its dissolving the quinoline hydrochloride formed, and in all cases, except where otherwise stated, the following procedure was adopted. The amine (0·05 gram-mol.) and 7 grams of quinoline were dissolved in 50—100 c.c. of dry chloroform, and 6 grams of chloroacetyl chloride diluted with 20 c.c. of chloroform added drop by drop, the whole being well shaken and the flask cooled under the tap or by immersion in ice-water. After keeping for one to two hours, the chloroform was removed by distillation from the water-bath, and the oily or pasty residue poured into cold, very dilute hydrochloric acid. After shaking for a few minutes, the chloroacetyl compound became solid and was then collected, washed with water, and recrystallised from water, alcohol, or from a mixture of these solvents.

In all cases, the pyridinium chlorides were very easily obtained by warming the chloroacetylamino-compound on the water-bath with about twice its weight of pyridine for half an hour. After cooling, the excess of pyridine was removed by washing with ether, and the pyridinium salt then recrystallised from a mixture of alcohol and ether, or, if not too soluble, from hot water. The chlorides crystallise extremely well, and as the chlorine is ionised and can be estimated by titration, the salts form a convenient method of identifying the amines. The picrates are sparingly soluble compounds, which are beautifully crystalline and easily obtained pure. They usually have sharp melting points.

It was thought of interest to prepare one or two pyridinium salts

from the chloroacetyl derivatives of the phenols, it being intended to extend this work to the chloroacetyl derivatives of the carbohydrates and more particularly of cellulose. Shortly after these experiments had been commenced, a paper appeared by another investigator (W. L. Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 253, 286T) dealing with the action of chloroacetyl chloride on cellulose in the presence of pyridine, and we have therefore abandoned our nvestigations in this direction for the present.

Acetanilide-ω-pyridinium chloride, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NCl{\vdots}C_5H_5$, forms colourless needles from a mixture of alcohol and ether, m. p. 245° (Found: Cl = 14·2. $C_{13}H_{13}ON_2Cl$ requires Cl = 14·3 per cent.). The *picrate* crystallises from hot water, in which it is moderately soluble, in lemon-yellow needles melting at 134° (Found: N = 16·3. $C_{19}H_{15}O_8N_5$ requires N = 15·9 per cent.).

*Aceto-*o*-toluidide-ω-pyridinium Chloride*,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NCl{\vdots}C_5H_5.$$

—The crude product was dried in a vacuum desiccator over concentrated sulphuric acid for four days, and the still soft mass dissolved in chloroform containing about 1 per cent. of alcohol. Ether was added to the filtered solution until it just became cloudy, and the whole cooled in ice. The compound melts at 187° (Found: Cl = 11·2. $C_{14}H_{15}ON_2Cl,3H_2O$ requires Cl = 11·2 per cent.). The *picrate* crystallises from hot water and melts at 171—172° (Found: N = 15·9. $C_{20}H_{17}O_8N_5$ requires N = 15·4 per cent.).

*Aceto-*p*-toluidide-ω-pyridinium chloride* crystallises from mixtures of alcohol and ether in pearly leaflets which melt at 239—243° (Found: Cl = 13·4. $C_{14}H_{15}ON_2Cl$ requires Cl = 13·5 per cent.). The *picrate* crystallises from boiling water in glistening, golden-yellow needles which sinter at 115° and melt at 141° (Found: N = 15·1. $C_{20}H_{17}O_8N_5,H_2O$ requires N = 15·1 per cent.).

m-*Nitroacetanilide-ω-pyridinium chloride*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NCl{\vdots}C_5H_5,$$

separates from hot water in almost colourless crystals which melt and decompose at 288—291° (Found: Cl = 11·6. $C_{13}H_{12}O_3N_3Cl,H_2O$ requires Cl = 11·4 per cent.). The *picrate* forms pale yellow needles which are but sparingly soluble in hot water and melt at 199—200° (Found: N = 17·6. $C_{19}H_{14}O_{10}N_6$ requires N = 17·3 per cent.).

p-*Nitroacetanilide-ω-pyridinium chloride* crystallises from hot water in hair-like, pale yellow needles which melt and decompose at 271—272° (Found: Cl = 11·9. $C_{13}H_{12}O_3N_3Cl$ requires Cl = 12·1 per cent.). The *picrate* resembles the chloride in appearance and is sparingly soluble in hot water. It sinters at 207° and melts at 211° (Found: N = 17·4. $C_{10}H_{12}O_{10}N_6$ requires N = 17·3 per cent.). The *nitrate* is precipitated when nitric acid is added to a solution of

the chloride, and although sparingly soluble is too soluble to be of any use for the gravimetric estimation of nitric acid.

Aceto-α-naphthalide-ω-pyridinium chloride,

$C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NCl{:}C_5H_5$,

separates from a mixture of alcohol and ether in colourless crystals which melt at 242° (Found: Cl = 11·7. $C_{17}H_{15}ON_2Cl$ requires Cl = 11·9 per cent.). The *picrate* separates from boiling water, in which it is very sparingly soluble, in glistening, yellow needles which melt at 228° (Found: N = 14·4. $C_{23}H_{17}O_8N_5$ requires N = 14·3 per cent.).

Aceto-β-naphthalide-ω-pyridinium chloride separates from a mixture of alcohol and ether in colourless crystals which melt at 240—241° (Found: Cl = 11·0. $C_{17}H_{15}ON_2Cl,2H_2O$ requires Cl = 11·2 per cent.). The *picrate* is very sparingly soluble in boiling water and melts at 174—175° (Found: N = 14·4. $C_{23}H_{17}O_8N_5$ requires N = 14·3 per cent.).

p-*Chloroacetylaminoazobenzene*, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, forms yellow crystals from boiling alcohol and melts at 154° (Found: N = 15·3. $C_{14}H_{12}ON_3Cl$ requires N = 15·3 per cent.). The *pyridinium chloride* crystallises from a mixture of alcohol and ether in small, yellow needles which melt and decompose at 250°. It has no tinctorial properties (Found: N = 15·8. $C_{19}H_{17}ON_4Cl$ requires N = 15·9 per cent.).

4-*Chloroacetylaminonaphthalene*-1-*azobenzene*,

$C_6H_5{\cdot}N{:}N{\cdot}C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$,

is best crystallised from methyl ethyl ketone and forms beautiful orange-red needles which melt at 217—218° (Found: N = 13·1. $C_{18}H_{14}ON_3Cl$ requires N = 13·0 per cent.). The *pyridinium chloride* is formed slowly and several hours' heating on the water-bath is necessary to prodnce it. It is best purified by dissolving the crude product in a large volume of boiling alcohol and concentrating the filtered solution to about half its volume. On adding ether and cooling in a freezing mixture, the chloride separates as glistening, orange-red needles which melt and decompose at 254°. It has no tinctorial properties (Found: N = 14·1. $C_{23}H_{19}ON_4Cl$ requires N = 13·9 per cent.).

p-*Chloroacetylaminophenyl chloroacetate*,

$CH_2Cl{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$,

is formed when *p*-aminophenol is treated with chloroacetyl chloride and quinoline in chloroform solution. It crystallises from aqueous alcohol in colourless, silky needles which melt at 170—171° (Found: N = 5·4. $C_{10}H_9O_3NCl_2$ requires N = 5·3 per cent.). As it is insoluble in cold dilute sodium hydroxide, one of the chloroacetyl groups has probably replaced the phenolic hydrogen atom. A pyridinium salt could not be obtained in a state of purity.

Acetyldiphenylamine-ω-pyridinium chloride,

$$(C_6H_5)_2N{\cdot}CO{\cdot}CH_2{\cdot}NCl{:}C_5H_5,$$

separates from a mixture of alcohol and ether as a colourless, crystalline powder which melts at 263—267° (Found: Cl = 10·6. $C_{19}H_{17}ON_2Cl$ requires Cl = 10·9 per cent.). The *picrate* is very sparingly soluble in hot water and forms small, yellow needles which melt at 225—226°. Several attempts were made to estimate the nitrogen, but in every case the substance exploded.

2-*Chloroacetylaminoanthraquinone*, $C_{14}H_7O_2{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$.—Ten grams of 2-aminoanthraquinone * were dissolved in 50 c.c. of boiling tetrachloroethane, and to the cooled solution 10 grams of chloroacetyl chloride and then 8 grams of quinoline were added. As soon as the quinoline was added the whole became warm and a clear solution was formed, from which yellow crystals were deposited on standing. After keeping over-night, these were collected with the aid of the pump, washed with ether, and recrystallised from ethyl or amyl alcohol. The resulting crystals were bright scarlet, and analysis showed that they contained about 20 per cent. of free aminoanthraquinone. By washing them rapidly with a large volume of warm acetone, this could be removed and the chloroacetylamino-compound obtained as a yellow powder which melted at 189—190° (Found: C = 63·9; H = 3·78. $C_{16}H_{10}O_3NCl$ requires C = 64·1; H = 3·33 per cent.). The *pyridinium chloride* is formed in the usual way by warming on the water-bath with pyridine. It is moderately soluble in hot water, but could not be obtained pure as, on cooling, it separates from its solutions in the colloidal state. The *nitrate* is much less soluble than the chloride and is precipitated when nitric acid is added to a solution of the chloride. It is easily soluble in boiling water, but the aqueous solution, on cooling, sets to a gel. It was recrystallised from dilute nitric acid and then formed an indistinctly crystalline powder which melted and decomposed at 265—267° (Found: N = 9·9. $C_{21}H_{15}O_6N_3,H_2O$ requires N = 9·9 per cent.). The *picrate* is almost insoluble even in boiling water and melts at 257—258°. It could not be crystallised, but a sample which had been well washed with hot water seemed to be pure (Found: N = 12·1. $C_{27}H_{17}O_{10}N_5$ requires N = 12·2 per cent.). The *dichromate* forms an insoluble, yellow powder which does not melt [Found: Cr = 11·6. $(C_{21}H_{15}O_3N_2)_2Cr_2O_7,6H_2O$ requires Cr = 11·7 per cent.].

Action of Chloroacetyl Chloride on Benzidine.—Attempts made to prepare a monochloroacetyl derivative of benzidine by treating benzidine in chloroform solution with chloroacetyl chloride, with or without the addition of quinoline, invariably led to a yellow product

* Kindly supplied by Scottish Dyes, Ltd.

which was completely insoluble in all the usual media and could not be recrystallised. The substance appeared to be quite unaffected by boiling with dilute sodium hydroxide solution, and its formation was probably due to both the chlorine atoms in the chloroacetyl chloride having reacted with the two amino-groups in benzidine.

By treating benzidine (9 grams) suspended in a large volume (500 c.c.) of dry ether with an ethereal solution of 6 grams of chloroacetyl chloride, the whole being well cooled in a freezing mixture, an impure product was obtained which appeared to contain a chloroacetyl derivative. This, when heated with pyridine (two parts) on the water-bath, gave a product which was partly soluble in alcohol. By precipitating the alcoholic extract with ether, a grey substance was obtained which decomposed too rapidly to allow of its purification. It was soluble in water, and by treating the aqueous solution with dilute hydrochloric acid and sodium nitrite and then pouring into an alkaline solution of β-naphthol, a deep red dye was obtained which was easily soluble in water. It was too unstable to be purified, and resinified in a few minutes.

Phenyl acetate ω-pyridinium chloride, $C_6H_5{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}NCl{:}C_5H_5$, is formed when phenyl chloroacetate is heated on the water-bath with an equal weight of pyridine. It crystallises from alcohol in colourless needles which melt and decompose at 165—168° (Found: Cl = 10·5. $C_{13}H_{12}O_2NCl,5H_2O$ requires Cl = 10·5 per eent.).

β-*Naphthyl acetate ω-pyridinium chloride*,

$$C_{10}H_7{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}NCl{:}C_5H_5,$$

is obtained in the same way as the phenyl compound. It forms colourless needles which melt and decompose at 169—170° (Found: Cl = 11·1. $C_{17}H_{12}O_2NCl,H_2O$ requires Cl = 11·0 per cent.).

o-*Acetoxybenzoic Acid ω-Pyridinium Chloride*,

$$CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}NCl{:}C_5H_5.$$

—Salicylic acid (14 grams) was converted into its chloroacetyl compound by boiling for three hours with an equal weight of chloroacetyl chloride dissolved in 80 c.c. of benzene. The solvent was then removed by distillation, and the pasty residue washed with light petroleum and several times with water. The resulting oil would not crystallise and was therefore converted into the pyridinium chloride in the usual way without further purification, and this, recrystallised from a mixture of alcohol and ether, formed colourless needles which melted and decomposed at 165—168° (Found: Cl = 10·8. $C_{14}H_{12}O_4NCl,2H_2O$ requires Cl = 10·8 per cent.).

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LXXXIX.—*The Action of Potassium Iodide and Iodate on some Hydroxy-acids.*

By Sri Krishna and Frank George Pope.

During the course of some work, Kux's method of estimating carboxyl (*Z. anal. Chem.*, 1893, **32**, 129) was applied to the case of salicylic acid and it was found that the amount of iodine liberated fell much below the quantity demanded by the equation $6R{\cdot}CO_2H + 5KI + KIO_3 = 6R{\cdot}CO_2K + 3I_2 + 3H_2O$, whilst a white or slightly coloured precipitate separated from the reaction mixture. The reaction was consequently further examined in the case of salicylic acid and some other aromatic hydroxy-acids.

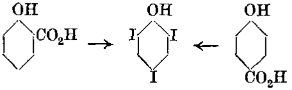
The method of procedure adopted consisted in adding a warm (50—80°) solution of the acid in small portions at a time to a warm aqueous solution of the iodide and iodate (in the proportions demanded by the above equation) and digesting the mixture on the water-bath for some time (usually about twenty minutes). During the addition process a considerable amount of iodine was liberated and in many cases carbon dioxide was apparently simultaneously evolved. After standing for the above time, it was found that the free iodine present had practically disappeared and that a faintly coloured precipitate had formed. This was collected, washed, recrystallised from a suitable solvent (usually benzene), and then further examined.

The reaction has been examined in the case of salicylic acid, *p*-hydroxybenzoic acid, 3- and 5-nitrosalicylic acids, and 3 : 5-dinitrosalicylic acid, and it has been found that in each case the carboxyl group has been eliminated and the corresponding tri-iodophenol produced; thus bringing the reaction into agreement with known cases, for it is well known that under certain experimental conditions halogens can replace the acidic groups in aromatic acids. Instances of this may be seen in the work of Datta and Bhowmik (*J. Amer. Chem. Soc.*, 1921, **43**, 303), who have shown that chlorine replaces the sulpho-group in sulphonic acids with simultaneous formation of chloro-derivatives, whilst Pope and Wood (T., 1912, **101**, 1827) showed that on brominating *p*-hydroxybenzoic acid in the presence of sulphuric acid some tribromophenol was also obtained.

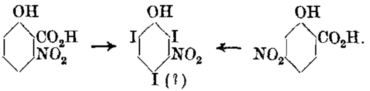
In the work of Datta and Bhowmik it was found that the replacement of the acid group takes place with ease in the case of chlorine and bromine, but only under special conditions with iodine, further halogen atoms then entering the complex. In this investigation

we have found that the action of potassium iodide and iodate on the hydroxy-acids was much more rapid than that of potassium bromide and bromate, and still more so than that of potassium chloride and chlorate.

The relative positions of the hydroxyl and carboxyl groups in the *simpler acids* seem to have no influence on the reaction, since the same product, namely, 2 : 4 : 6-tri-iodophenol is obtained from either salicylic acid or *p*-hydroxybenzoic acid :



and the same tri-iodonitrophenol from either 3- or 5-nitrosalicylic acid :



3 : 5-Dinitrosalicylic acid yields similarly a tri-iododinitrophenol. β-Resorcylic acid apparently reacts in a normal manner, as does *o*-acetoxybenzoic acid.

The reaction was also extended to anthranilic acid and to acetylanthranilic acid, and in these cases direct substitution by iodine appears to take place without elimination of the carboxyl group.

The identity of the products was in most cases determined by observing the mixed melting points obtained with the same compound, prepared according to one of the already known methods.

EXPERIMENTAL.

Salicylic Acid.—Two grams of salicylic acid were dissolved in 25 c.c. of water, the solution warmed to 50° and added in small quantities to an aqueous solution of 10 grams of potassium iodide and 2 grams of potassium iodate, also at 50°. Iodine was liberated and carbon dioxide evolved. The mixture was kept for twenty minutes on the water-bath, the precipitate collected, washed, dissolved in a dilute solution of sodium hydroxide, and reprecipitated by the addition of dilute hydrochloric acid. It was again collected, washed, dried, and finally crystallised from benzene, from which it separated in long, colourless needles melting at 158°; it thus appears to be 2 : 4 : 6-tri-iodophenol. A specimen mixed with tri-iodophenol showed no depression of melting point (Found : I = 80·30. Calc., I = 80·72 per cent.).

p-Hydroxybenzoic acid was treated in exactly the same manner, similar quantities being used. The product obtained was identified as tri-iodophenol.

3-*Nitro- and* 5-*nitro-salicylic acids*, by the same method of treatment, gave a precipitate of fine, red needles of the potassium salt of a tri-iodonitrophenol. This was collected, dissolved in water, and decomposed by hydrochloric acid. The phenol obtained was recrystallised from benzene, from which it separated in shining, yellow plates melting at 148°. From the analytical data obtained it would appear to be a tri-iodonitrophenol, possibly 2 : 5 : 6-tri-iodo-3-nitrophenol (Found: I = 73·44; N = 2·92. Calc., I = 73·69; N = 2·70 per cent.).

3 : 5-*Dinitrosalicylic acid*, by a similar process, deposited red needles of the potassium salt of a tri-iododinitrophenol. The salt was dissolved in water, and on acidification of the solution the phenol was obtained. It was recrystallised from benzene (or toluene) and separated in glistening plates which melted at 165° (Found: I = 67·42; N = 4·74. Calc., I = 67·79; N = 4·98 per cent.).

Anthranilic Acid.—Using the same method in the case of anthranilic acid, it was found that the solution remained clear after warming, but on the addition of a few drops of hydrochloric acid a lemon-yellow precipitate was thrown down. This was collected, washed, dried, and recrystallised from benzene, separating from the solvent in needles melting at 208°. It would thus appear to be identical with (β)-3-iodo-2-aminobenzoic acid, melting at 208—209°, since no depression of melting point was observed when the two compounds were mixed (Found: I = 48·03; N = 5·22. Calc., I = 48·28; N = 5·32 per cent.).

Acetylanthranilic acid behaves in the same manner, a brown precipitate being obtained on warming the solution. This was collected, washed, dissolved in dilute sodium carbonate solution, and reprecipitated by the addition of hydrochloric acid. The product was collected, dried, and recrystallised from benzene, from which it separated in colourless, shining plates melting at 175°. It is apparently an iodoacetylanthranilic acid (Found: I = 41·40. $C_9H_8O_3NI$ requires I = 41·50 per cent.).

It is hoped to continue the work and to characterise the iodophenols obtained. One of us (S.K.) desires to express his thanks to the Committee of Scientific and Industrial Research for a grant that has helped to defray expenses.

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XC.—*Mixed Crystal Formation in Ternary Systems containing Water, Ammonium Chloride, and Ferrous, Cobaltous, or Nickel Chloride.*

By FREDERICK WILLIAM JEFFREY CLENDINNEN.

THE relationships found in the system ammonium chloride–manganous chloride–water (Clendinnen and Rivett, T., 1921, **119**, 1329) have suggested the advisability of a comparative study of those cases in which bivalent manganese has been replaced by bivalent iron, cobalt, or nickel, neighbouring members of the same series in the periodic classification. The present paper gives the experimental results which have been obtained. For brevity, double salts will be indicated, as before, by adjacent numerals giving the relative numbers of formula weights of components in the order NH_4Cl, MCl_2, and H_2O.

A certain amount of work has previously been carried out by other observers, but none of it is sufficiently complete. The cobalt and nickel systems have been studied most, and a double salt 1 : 1 : 6 has been described for each case. The chief references are to Adams and Merrick (*Chem. News*, 1872, **25**, 187), Mitchell (*Arch. Pharm.*, 1876, **209**, 178), Chassevant (*Ann. Chim. Phys.*, 1893, [vi], **30**, 5), Johnsen (*Jahrb. Min.*, 1903, **2**, 93), and Foote (*J. Amer. Chem. Soc.*, 1912, **34**, 880).

Foote (*loc. cit.*) worked at 25°, but did not complete the isotherm for either system. He showed that a series of mixed crystals composed of ammonium chloride and the dihydrate of the metallic chloride is formed in each case. The appearance of the hexahydrates as stable phases at 25° cuts off the mixed crystal formation at one end just as did the appearance of manganous chloride tetrahydrate at the same temperature in the other case (Clendinnen and Rivett, *loc. cit.*, Fig. 2, p. 1333).

Very little indeed has been done on the system containing ferrous chloride. An anhydrous double salt 2 : 1 : 0 has been mentioned by a number of workers. Friend's "Text-book of Inorganic Chemistry" gives the following references: Winkler, *Rep. Pharm.*, 1836, **59**, 171. See also Hisinger and Berzelius, *Gilbert's Annalen*, 1807, **27**, 273; Vogel, *J. pr. Chem.*, 1834, **2**, 192; Chassevant, *loc. cit.*

To study the mixed crystals series, it is necessary to choose a temperature above that at which hydrates higher than the dihydrate appear; 60° has been chosen for the cobalt and 70° for the nickel and iron systems. As a matter of fact, the transition points

Table I.

System NH_4Cl–$FeCl_2$–H_2O at 70°.

Percentage Composition.

	Solution.		Residue.		Solid. (Extrapolated)	
sity.	NH_4Cl.	$FeCl_2$.	NH_4Cl.	$FeCl_2$.	NH_4Cl.	
162	31·39	9·52	68·90	10·22	86·0	
213	27·78	15·03	61·50	16·86	77·1	
260	24·24	19·78	43·59	21·35	69·3	
—	21·60	23·25	39·28	27·79	57·9	
307	19·97	25·22	39·95	33·35	50·9	
318	18·61	26·56	34·68	34·44	47·4	
338	17·04	28·38	33·20	37·69	43·6	
350	16·02	29·49	33·06	40·20	41·2	
362	14·99	30·53	30·08	40·01	40·0	
377	13·78	31·89	28·92	41·09	38·9	
404	11·73	34·19	25·51	41·72	37·7	
420	10·23	36·05	23·93	42·45	37·1	
450	8·75	38·29	24·33	45·18	35·3	
475	7·28	40·72	19·05	46·75	31·6	
479	6·76	41·18	20·54	50·75	28·0	
470	6·72	41·37	17·44	49·55	26·5	
477	6·87	41·22	16·69	49·84	25·7	
485	6·28	41·98	15·76	50·85	24·1	
—	5·29	43·02	13·85	53·13	20·8	
520	4·19	44·71	11·55	54·48	18·0	
—	3·27	45·61	6·95	55·32	11·6	
—	2·69	46·42	5·38	59·46	8·0	
—	1·64	46·69	0·46	59·40		}
533	1·33	46·66	0·40	58·96		} $FeCl_2,4H_2O$
527	—	46·90	—	—		}

Table II.

System NH_4Cl–$CoCl_2$–H_2O at 60°.

Percentage Composition.

	Solution.		Residue.		Solid. (Extrapolated)	
Density.	NH_4Cl.	$CoCl_2$.	NH_4Cl.	$CoCl_2$.	NH_4Cl.	
1·164	29·10	10·11	83·10	3·67	96·2	
1·240	25·25	17·53	69·82	11·19	88·8	
—	22·96	21·98	48·52	19·78	78·0	
1·329	21·32	25·86	55·16	25·65	67·6	
1·363	19·09	29·67	45·43	31·15	59·0	
1·362	18·15	30·66	45·15	33·38	55·8	
1·380	17·74	31·24	41·23	35·20	52·7	}
1·403	16·99	32·28	46·63	37·45	51·2	}
—	14·96	34·84	33·05	39·68	45·2	} Metastable.
—	14·05	35·98	29·47	41·57	41·1	}
1·454	13·08	37·05	33·02	46·85	37·9	}
1·476	11·71	38·96	25·17	45·25	35·7	}
—	10·50	39·94	23·34	47·31	32·7	
1·482	10·36	40·14	21·05	47·17	31·0	
—	—	—	20·44	46·46	31·5	
—	10·36	40·14	22·67	47·96	31·5	
1·504	9·04	41·42	18·98	48·00	29·4	
1·530	6·90	43·56	17·44	52·45	25·0	
1·559	5·02	45·74	11·68	52·11	21·2	
—	3·69	47·41	13·02	59·02	17·4	
1·580	3·44	47·44	8·00	57·55	12·7	
—	3·12	47·58	7·23	63·30	9·3	
1·575	2·59	48·06	6·15	63·98	8·0	
1·592	2·21	48·21	4·15	59·20	6·7	
1·587	1·79	48·37	2·12	60·52	2·6	
1·585	0·90	48·62	1·01	61·10	1·1	
—	—	48·84	—	—	—	
—	16·87	30·94	23·81	36·13	40·0	
—	15·64	32·28	24·40	37·76	40·0	
1·401	14·21	33·66	29·59	41·86	40·0	
1·414	13·57	34·36	24·75	40·44	38·8	
—	12·93	35·02	30·81	43·90	38·8	

Table III.

System NH_4Cl–$NiCl_2$–H_2O at 70°.

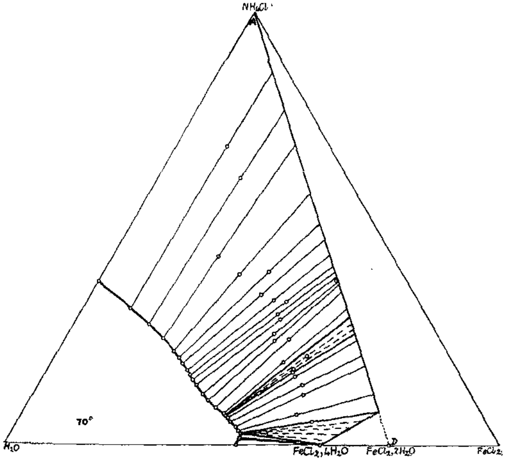
Percentage Composition.

	Solution.		Residue.		Solid. (Extrapolated)
Density.	NH_4Cl.	$NiCl_2$.	NH_4Cl.	$NiCl_2$.	NH_4Cl.
1·162	30·92	8·59	75·46	3·69	98·3
1·234	26·09	15·83	80·08	6·80	94·6
1·294	22·91	21·29	65·20	11·24	93·9
1·355	20·47	26·28	60·22	15·42	84·6
1·386	19·01	28·96	52·28	23·04	75·1
1·401	18·37	30·03	47·43	26·71	68·8
1·411	17·54	30·69	43·38	29·70	62·5
1·409	17·57	30·70	44·85	32·42	57·2
1·421	16·93	31·31	36·45	34·34	52·5
1·426	16·24	32·30	35·26	37·07	48·0
1·446	15·05	33·54	28·40	37·63	45·1
1·469	13·56	35·22	31·12	43·46	39·3
1·492	11·74	36·99	22·63	43·31	34·8
1·510	10·09	38·88	21·88	46·82	31·4
1·530	8·43	40·43	21·53	50·60	28·1
1·552	6·96	42·05	19·27	52·03	25·9
—	5·35	43·87	12·63	51·12	21·8
1·591	4·62	44·70	2·12	65·70	0·9
1·587	2·79	44·99	1·45	63·38	0·4
1·589	1·24	45·60	0·61	64·99	0·1
1·592	—	45·80	—	—	—

between the various hydrates of ferrous chloride have not been accurately determined, and although, according to figures in Landolt-Börnstein-Roth Tables, the dihydrate is the stable phase at 70°, *it has been found that the tetrahydrate is still stable at this* temperature, although fortunately it obscures only a small portion of the mixed crystal series.

The experimental procedure has been similar to that in the previous work on the manganous system (*loc. cit.*). Tables I, II, and III give the results which have been obtained, and in Figs. 1,

FIG. 1.



2, and 3 these results are plotted in the customary triangular method.

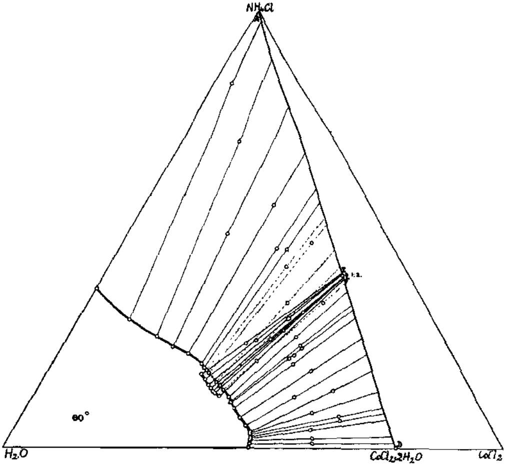
With regard to the compositions of the mixed crystals in these systems, Foote's work (*loc. cit.*) indicates that they can be represented by points on the lines *AD* at 25°. Analysis of several dried samples confirms this for the higher temperatures.

It is seen that the ferrous system (Fig. 1) is very similar to the manganous system; if, however, the 70°-isotherm of the former is compared with the 60°-isotherm of the latter, it is observed

that one of the gaps in the series of solids, namely, that near the ammonium chloride end, of the manganous system has no counterpart in the ferrous system, there being an unbroken series of solids in this region. It is thought probable that this difference will disappear if the comparison is made at corresponding temperatures.

A comparison between the ferrous system at 70° and the cobalt at 60° shows a similar difference : here it is the second gap in the solid series which is involved, the mixed crystal series in the cobalt

FIG. 2.

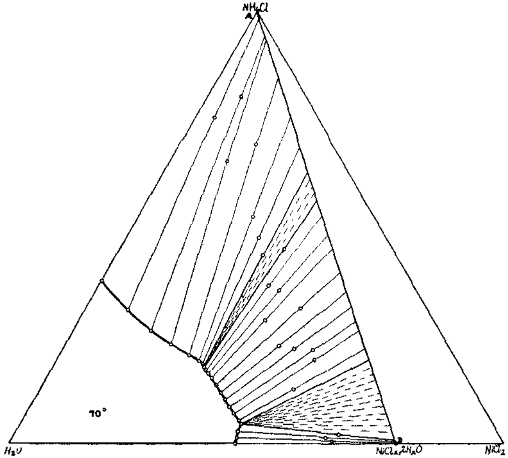


system at 60° being continuous from ammonium chloride to cobalt chloride dihydrate, corresponding with a continuous solubility curve.

For a part of this series, however, shown with dotted tie lines in Fig. 2, the system is metastable, although easily attained. The stable state is that of a series of solutions in equilibrium with a mixed crystal series having the very limited range of composition *EF*. It will be seen that the composition corresponding with 2 : 1 : 2 lies within this range. The metastable portion of the main

curve was obtained by removing the mixtures from the thermostat two hours after their immersion. Mixtures of similar composition to these, when rotated in the thermostat for upwards of one day, were found to have resolved themselves into solutions on the second curve and solids in the new state. It was found impracticable

FIG. 3.



to determine completely this stable curve, owing to the long time necessary for the change from metastable to stable at points close to the intersections of the two curves.

The results of a closer investigation of these and of other closely allied systems will be given in a later communication.

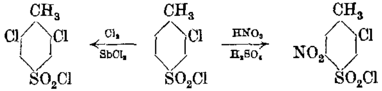
In conclusion, I desire to express my thanks to Dr. A. C. D. Rivett, whose criticism was invaluable throughout.

UNIVERSITY OF MELBOURNE. [*Received, March* 3*rd*, 1922.]

XCI.—*An Instance of the Apparent Effect of the Entering Group on the Position of Substitution in the Benzene Nucleus.*

By William Davies.

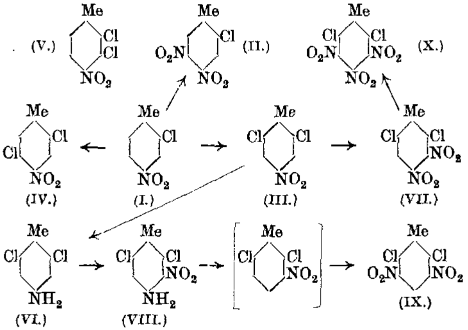
It is usually considered that in substitutions in aromatic compounds the position taken up by a new group is almost independent of the nature of that group. Whilst this assumption seems to be justified in simple cases, there is reason to believe that the effect of the nature of the new substituent may in complicated cases be far from negligible. For example, it has been shown (Davies, T., 1921, **119**, 859) that nitration and chlorination of 2-chloro-*p*-toluenesulphonyl chloride lead respectively to the 5-nitro- and the 6-chloro-derivatives as chief products.



(XII.)

With the object of providing, if possible, a basis for generalisation, the comparative effects of the nitration and chlorination of 2-chloro-4-nitrotoluene (I) have been studied. This substance was chosen both because of its analogy to 2-chloro-*p*-toluenesulphonyl chloride and because it has already been nitrated by Morgan and Drew (T., 1920, **117**, 793), who showed that (II) was produced in a yield of more than 85 per cent. The experimental portion of this paper is concerned with the chlorination of (I) under conditions approximating as closely as possible to those obtaining in the nitration (Morgan and Drew, *loc. cit.*), and it has been found that the expected irregularity has again occurred, a comparatively large proportion of (III) being formed. It has unfortunately not been possible to find the exact proportion of the isomerides produced, but the isomeride which crystallises at the ordinary temperature in a yield exceeding 30 per cent. is (III). The melting point of this substance is 65°. Since this value is only slightly higher than the melting points (50—51° and 51° respectively) of the other two possible isomerides (IV) and (V) (compare Cohen, T., 1901, **79**, 1130; Cohen and Dakin, T., 1902, **81**, 1327), it is very probable that the separation of (III) in such large amount indicates that this is the chief product.

The chemistry of (III) and of its simpler derivatives, and at the same time the proof of the formula assigned to it, are indicated in the following diagram.



Additional evidence in favour of formula (III) assigned to the dichloro-*p*-nitrotoluene isolated is to be found in a consideration of the melting points of the corresponding toluidines. The melting points of the amino-derivatives from (IV) and (V) are 91—92° and 40—42°, respectively (Cohen, and Cohen and Dakin, *loc. cit.*). The amino-derivative (VI) described in the present communication melts at 56—57°.

The literature does not seem to supply any analogous instances of the entering group apparently affecting the position of substitution. Beilstein and Kuhlberg (*Annalen*, 1868, **146**, 327), indeed, claimed that the chlorination of benzal chloride and of benzotrichloride in the presence of iodine resulted in the production of para-chloro-derivatives, whilst nitration with concentrated nitric acid led to meta-nitro-derivatives. This statement, at any rate as far as benzotrichloride is concerned, is not borne out by recent experiments. By nitrating with nitrogen pentoxide in carbon tetrachloride, Spreckles (*Ber.*, 1919, **52**, 315) obtained *m*-nitrobenzotrichloride as chief product, but by chlorination in the presence of iodine a mixture of isomerides was formed, and it was not possible to find the one occurring in greatest amount.

A possible explanation of the difference in the position of substitution in the nitration and chlorination of (I) may be ascribed to the presence of a catalyst in the latter reaction. Since position

isomerides are rarely, if ever, in true equilibrium, it is quite conceivable that a certain catalyst may accelerate the formation of one isomeride at the expense of another. With the view of testing this hypothesis, the chlorination of 2-chloro-4-nitrotoluene in the presence of different catalysts has been studied. If the hypothesis is correct, it is to be expected that the proportion of "favoured" isomeride will not be independent of the nature of the catalyst.

The comparative experiments carried out did naturally not admit of very exact treatment, but it was shown that the proportion of (III) separating out of the reaction product was the same, within the limits of experimental error, when ferric chloride and when antimony trichloride were the catalysts. The use of aluminium amalgam resulted in the composition of the product of reaction approaching more closely to that of a eutectic mixture. The greatest difference was obtained when iodine was the catalyst. In this case, however, some substitution in the side chain had apparently taken place, and this unexpected result brought these comparative experiments to a close, with the effect of the catalyst on substitution still in doubt. It is hoped that this important point will be studied in the near future with the aid of aromatic substances containing no side chain.

It must be pointed out that the conditions of nitration and chlorination are at first sight scarcely comparable, for sulphuric acid is used in the first process but not in the second. The action of sulphuric acid in affecting the position of substitution apparently depends, however, on the initial formation of a salt (compare Armstrong, T., 1887, **51**, 589; Morgan and Clayton, T., 1910, **97**, 2649). Henee, as neither 2-chloro-4-nitrotoluene nor 2-chloro-*p*-toluenesulphonyl chloride contains a basic group, it is extremely improbable that the sulphuric acid has any directive effect in these particular instances.

The effect of the catalyst and the nature of the entering substituent are the remaining possible explanations, and the author is of the opinion that the first is the correct one. Assuming that the difference found in chlorinating (I) in the presenee of antimony trichloride and of iodine is altogether due to the entry of chlorine in the side chain when iodine is the catalyst, then it is extremely probable that the position of nuclear substitution will also, in these complex cases, depend to a considerahle extent on the catalyst employed. It may thus be possible to obtain one or other of two position isomerides as chief product in chlorination, according to the catalyst used.

Whilst admitting the probable effect of the catalyst, it must be borne in mind that in complicated cases such as those under dis-

cussion, where the influences of the substituents act more or less against each other and doubtless more or less neutralise each other, it is to be expected that the influence of the nature of the entering group will be comparatively large. Two independent theories which have recently appeared (Vorländer, *Ber.*, 1919, **52**, 263; Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1) agree in regarding nitroxyl and halogens as possessing opposite polarity. This view may afford an explanation of the difference in position of substitution in the chlorination and the nitration of (I) and (XII). A logical explanation cannot be found by a consideration of the difference of molecular volume between a nitro-group and a chlorine atom. For example, although a nitro-group has a larger volume than a chlorine atom (Le Bas, "The Molecular Volumes of Liquid Chemical Compounds," 1915, p. 249), nevertheless in the nitration of 2-nitro-*p*-toluenesulphonyl chloride (Reverdin and Crepieux, *Ber.*, 1901, **34**, 2992) and of 2 : 4-dinitrotoluene, the entering nitro-group occupies the 6-position in both cases, and this is the same position relative to the methyl group that is mainly occupied by chlorine in the chlorination of (I) and (XII).

In this connexion reference must be made to a statement in a recent paper (Fraser, this vol., p. 188) dealing with the structure of the benzene molecule. It is there claimed (pp. 195, 196) that substituents of small volume such as hydroxyl- and amino-groups tend to direct to the ortho- and para-positions, and, on the other hand, substituents of large volume such as the nitro- and sulpho-groups direct to the meta-positions. Such a statement is misleading. The nitration of *tert.*-butylbenzene (Malherbe, *Ber.*, 1919, **52**, 319) and of *p*-toluenesulphon-*o*-toluidide (Morgan and Challenor, T., 1921, **119**, 1544) leads almost entirely to derivatives in which the nitro-group occupies the para- and not the meta-position to the substituent which has a molecular volume (Le Bas, *op. cit.*) about as large as that of benzene itself. Many other similar authenticated instances, such as the nitration of acyl-substituted amino- and hydroxy-derivatives of benzene, indicate that the "polarity" (Lapworth, *loc. cit.*; *Annual Reports*, 1919, **16**, 89) and not the volume of the substituent is the deciding factor in substitution. It may very well be that in vicinal tri- and tetra-substituted benzene derivatives the volumes of the groups will have considerable effect on the position of substitution; but it has yet to be proved that Fraser's statement holds for monosubstituted benzene derivatives.

EXPERIMENTAL.

2-Chloro-4-nitrotoluene was obtained by the chlorination at 65—75° of *p*-nitrotoluene containing 5 per cent. of antimony tri-

chloride until the increase in weight corresponded with monochlorination. The product was freed from antimony trichloride as in the preparation of 2-chloro-*p*-toluenesulphonyl chloride (Davies, *loc. cit.*, p. 860), when 2-chloro-4-nitrotoluene, boiling at 257—260°/756 mm. and melting at 62—65°, was obtained in a yield of 95 per cent.

2-Chloro-4-nitrotoluene (233 grams) was mixed with antimony trichloride (16·5 grams) and chlorinated at 60—70° until the increase in weight (45·8 grams) corresponded with the entrance of one atom of chlorine. The reaction took place very smoothly and the heat developed was sufficient to keep the mixture at the temperature stated. When allowed to remain at the ordinary temperature, the product partly solidified, and after three days the solid was collected. It consisted of slightly impure 2 : 6-dichloro-4-nitrotoluene melting at 54—62°, and weighed 87 grams (31·2 per cent. of theory). When crystallised from alcohol, it melted at 63—65°.

The liquid portion of the product was separated from antimony trichloride and hydrochloric acid in the usual way, and distilled at 757 mm. The first fraction (15 grams), b. p. 261—267°, contained a large proportion of unchanged 2-chloro-4-nitrotoluene. The other fraction (125 grams) boiled at 267—280°, and on remaining at the ordinary temperature for several days deposited about 12 grams of rather impure 2 : 6-dichloro-4-nitrotoluene.

It may be noted that when *p*-nitrotoluene is dichlorinated under conditions similar to those described above, slightly impure 2 : 6-dichloro-4-nitrotoluene crystallises out in a yield of more than 30 per cent.

Various attempts were made to separate the mobile mixture of isomerides boiling at 267—280°/757 mm. Distillation, fractional distillation in steam, and crystallisation were found to be useless. Since it is to be expected that 2 : 5-dichloro-4-nitrotoluene would be more readily oxidised than 2 : 6-dichloro-4-nitrotoluene, the separation by preferential oxidation with boiling potassium permanganate solution in presence of carbon dioxide was attempted, but a negative result was obtained. Boiling the mixture with aniline with the object of converting the 2 : 5-dichloro-derivative (which contains a chlorine atom ortho to a nitro-group) into 2-chloro-4-nitro-5-phenylaminotoluene was also unsuccessful, as it was impossible to obtain a crystalline substance from the tar produced. Separation by means of sulphuric acid as solvent was also found to be unsatisfactory.

The Effect of Different Catalysts on the Chlorination of 2-Chloro-4-nitrotoluene.

Catalyst. Wt. in grams.	Time of chlorination in minutes.	Increase in wt. (i) at the end of the reaction. (ii) after remaining for 48 hrs. over NaOH in a vacuum at 5–10°.	Wt. of precipitate (dried on porous plate) deposited in 48 hrs at 5–10°.	M. p. of precipitate and percentage wt. (neglecting catalyst) of the product.	Observations.
Antimony trichloride. 2·0	130	(i) 23 (ii) 21·5	47·5	54–62° 35	The product was clear red.
Ferric chloride. 2·0	95	(i) 24 (ii) 22·5	45·5	54–62° 33·3	The product was brown and opaque.
Aluminium amalgam. 2·0	115	(i) 23·7 (ii) 22	52·5	30–55° 38·5	The warm brown product was poured from the apparently unchanged catalyst.
Iodine. 1·5	90	(i) 24 (ii) 23·5	None		The product was clear red.

In each of these comparative experiments two-thirds of a gram-mol. (114·3 grams) of the same sample of 2-chloro-4-nitrotoluene (b. p. 257—260°/756 mm.) was chlorinated in diffused daylight at 60—70° until the increase in weight (23 grams) corresponding with monochlorination was attained as closely as possible. In every case, chlorination took place most readily at first. It is noteworthy that the chlorination product dissolved (except when iodine was the catalyst) a considerable amount of hydrogen chloride. A portion of the isomeride crystallising out in each case was purified and shown to be 2 : 6-dichloro-4-nitrotoluene by determining the melting point when mixed with an authentic specimen of this substance.

In the first two experiments no attempt was made to separate the small amount of catalyst used, which remained in the liquid portion of the product. In the experiment with aluminium amalgam, the chlorination product set to a viscous mass almost like a gel, and it was impossible to filter it in the ordinary way. The solid portion was obtained by allowing the mass to remain on a large porous plate for twenty-four hours, when the oil was gradually absorbed. The solid portion was extremely impure, as was shown by the melting point and by the fact that a large proportion of oil was produced during crystallisation from alcohol.

With iodine as catalyst, the liquid product, after remaining for two days, was washed successively with water, a solution of sodium hydrogen sulphite, and water, and extracted with benzene, the extract being then dried over sodium sulphate and the benzene

removed. The clear red residual oil, which fumed a little in air despite the thorough washing and drying, was separated into two fractions, b. p. 273—283° (80 grams) and 283—295° (25 grams); hydrogen chloride was produced in the distillation of both fractions, and the residue in the flask began to decompose vigorously. Moreover, the second fraction was not produced when the reaction liquid with antimony trichloride as catalyst was distilled (see above). These facts seem to indicate that the toluene derivative had, when iodine was the catalyst, been chlorinated to a certain extent in the side chain.

The first fraction, after remaining for twenty-four hours at 5—10°, deposited 1·85 grams of impure 2 : 6-dichloro-4-nitrotoluene melting at 56—61°. The chlorination was repeated with 2·0 grams of iodine, and the results were almost identical with those obtained when 1·5 grams of iodine were used.

When this series of experiments was begun, it was not anticipated that the chlorine, under the conditions of the experiment, would enter the side chain at all. Iodine is generally regarded as a catalyst for introducing chlorine into the nucleus only.* Since the formation of a relatively small proportion of the benzyl chloride derivative might affect very considerably the proportion of 2 : 6-dichloro-4-nitrotoluene separating out from the chlorination product, this investigation was brought to a close with the question at issue still unsolved.

2 : 6-*Dichloro*-4-*nitrotoluene* (III) crystallises from alcohol or light petroleum (of high b. p.) in thick, colourless, faintly odorous, blunt needles, which melt at 65° and boil without decomposition at 278—279°/760 mm. (Found: Cl = 34·05. $C_7H_5O_2NCl_2$ requires Cl = 34·46 per cent.). It is very stable towards potassium permanganate solution, no derivative of benzoic acid being produced after boiling for six hours in the presence of carbon dioxide (which was used to reduce the formation of stilbene derivatives to a minimum).

2 : 6-*Dichloro*-3 : 4-*dinitrotoluene* (VII).—2 : 6-Dichloro-4-nitrotoluene (5 grams), mixed with 10 c.c. of nitric acid (*d* 1·5) and 10 c.c. of concentrated sulphuric acid, was heated with frequent shaking on the water-bath for an hour, when crystals rapidly separated in the hot solution. The nitration mixture was poured into water, and the precipitate (5·2 grams) crystallised from alcohol. 2 : 6-*Dichloro*-3 : 4-*dinitrotoluene* is moderately soluble in boiling and slightly soluble in cold alcohol, from which it separates in long,

* Compare Weyl, "Methoden der Organischen Chemie," vol. ii, p. 1066. In this *connexion, it should be noticed that* "ähnlich" (*loc. cit.*, p. 1069, second line from the bottom) is a mistake for "nicht ähnlich."

colourless, odourless needles melting at 130—131° (Found: N = 11·2. $C_7H_4O_4N_2Cl_2$ requires N = 11·1 per cent.).

2 : 6-*Dichloro*-p-*toluidine* (VI).—A mixture of 2 : 6-dichloro-4-nitrotoluene (15 grams) with water (150 c.c.) and finely divided iron filings (60 grams) was heated under reflux at 95°, removed from the water-bath, treated with concentrated hydrochloric acid (10 c.c.), and well shaken. A vigorous reaction soon set in, and a further 15 grams of the nitro-compound were added at such a rate that the ebullition was maintained. The reduction was almost finished in a quarter of an hour, and was completed by heating for an hour on the water-bath. The product was filtered hot, and the precipitate extracted with a little hot alcohol, which was added to the filtrate. The oily solution in the filtrate rapidly solidified on cooling to a pale yellow solid (16 grams), which was collected. The yield can be increased to 22 grams by treatment of the filtrate and unchanged iron with alkali and subsequent distillation in steam.

2 : 6-*Dichloro*-p-*toluidine* crystallises from dilute alcohol or light petroleum in colourless needles melting at 56—57° (Found: N = 7·9. $C_7H_7NCl_2$ requires N = 7·9 per cent.). It is extremely soluble in alcohol and slightly volatile in steam. Its faint smell recalls that of *p*-toluidine. The *hydrochloride* is readily soluble in hot and sparingly soluble in cold water, from which it separates in long, colourless needles. The *acetyl* derivative, obtained in the usual way, crystallises from dilute alcohol in colourless, slender needles melting at 220° (Found: N = 6·2. $C_9H_9ONCl_2$ requires N = 6·4 per cent.).

2 : 6-*Dichlorotoluene*-4-*azo*-β-*naphthol*, produced as a crimson powder by adding the dilute hydrochloric acid solution of 2 : 6-dichlorotoluene-4-diazonium hydrochloride to an alkaline solution of β-naphthol, crystallised from glacial acetic acid in minute, crimson rods melting at 243°. It is slightly soluble in boiling acetic acid and in boiling alcohol (Found: N = 8·03. $C_{17}H_{12}ON_2Cl_2$ requires N = 8·45 per cent.).

2 : 6-*Dichloro*-3-*nitro*-p-*toluidine* (VIII).—Finely powdered 2 : 6-dichloroaceto-*p*-toluidide (6 grams) was slowly added to nitric acid (30 c.c.; *d* 1·49) cooled in ice water. The nitration liquid was stirred after each addition until complete solution took place, the experiment being of an hour's duration. The clear red solution was poured into water, and the white, flocculent mass (7·9 grams) collected and crystallised from alcohol. In this way 2 : 6-*dichloro*-3-*nitroaceto*-p-*toluidide* was obtained in colourless needles (m.p. 180°), difficultly soluble in cold and moderately soluble in hot alcohol. When heated with sodium hydroxide solution, a green coloration

was formed, which was rapidly replaced by a red coloration (Found: N = 19·5. $C_9H_8O_3N_2Cl_2$ requires N = 19·6 per cent.).

Hydrolysis was effected by boiling this acetyl derivative for twenty minutes with a slight excess of alcoholic sodium hydroxide and then diluting the solution with an equal volume of water. An excellent yield of 2 : 6-*dichloro*-3-*nitro*-p-*toluidine*, minute, orange needles melting at 130—131°, was obtained (Found: N = 12·5. $C_7H_6O_2N_2Cl_2$ requires N = 12·7 per cent.).

The *hydrochloride*, which is produced from the free base by boiling with a large excess of concentrated hydrochloric acid, consists of clusters of colourless needles. It is sparingly soluble in concentrated hydrochloric acid and is at once hydrolysed by cold water.

*Conversion of 2 : 6-Dichloro-3-nitro-*p*-toluidine into 2 : 6-Dichloro-3 : 5-dinitrotoluene* (IX).—A cold solution of 2 : 6-dichloro-3-nitro-*p*-toluidine (2·2 grams) in alcohol (40 c.c.) was treated with concentrated sulphuric acid (3 c.c.) and then with a solution of sodium nitrite (1·2 grams) in 4 c.c. of water. The mixture was heated on the water-bath until effervescence had ceased, the acetaldehyde and most of the alcohol distilled off, and the product poured into water. The red oil, which rapidly solidified but did not melt sharply, was extracted with warm 50 per cent. sulphuric acid (in order to remove any unchanged amine), and the remaining dichloronitrotoluene heated with a mixture of nitric and sulphuric acids on the water-bath for ten minutes, the product poured into water and crystallised from alcohol and from light petroleum, when it was obtained in colourless needles melting at 121°. It was shown to be identical with 2 : 6-dichloro-3 : 5-dinitrotoluene (m. p. 120—121°) by a mixed melting-point determination.

2 : 6-*Dichloro*-3 : 4 : 5-*trinitrotoluene* (X).—With the object of preparing a derivative of 2 : 6-dichlorotoluene in which both the chlorine atoms would be in the ortho- and para-positions to two nitro-groups, and so might be replaceable by amino- or other groups—and therefore might serve for the identification of any 2 : 6-halogenotoluene—the continued nitration of 2 : 6-dichloro-3 : 4-dinitrotoluene was investigated. Vigorous measures were required for the introduction of the third nitro-group. 2 : 6-Dichloro-3 : 5-dinitrotoluene (5 grams) was heated with a mixture of 3 c.c. of nitric acid (*d* 1·5) and 10 c.c. of fuming sulphuric acid (20 per cent. SO_3) at 140—150°, with frequent shaking, for six hours. The product was poured into water, the precipitate (about 5 grams) collected and crystallised from alcohol, from which it separated in small needles melting at 145—155°. Crystallisation from alcohol did not appreciably affect the melting point. The substance was accordingly nitrated once more under similar conditions, the

temperature, however, being at 155—165°, and the product worked up as before. In this way an odourless substance was obtained, slightly soluble in cold alcohol or light petroleum (b. p. 80—100°), very soluble in benzene or acetone, and readily soluble in hot alcohol, from which it separated in small, colourless needles melting at 160—163° (Found: N = 14·7. $C_7H_3O_6N_3Cl_2$ requires N = 14·2 per cent.).

This trinitro-derivative was heated for an hour on the water-bath with excess of alcoholic ammonia, which reacted even in the cold. The dark red solution was evaporated to dryness, and thus found to have contained ammonium nitrite, but no appreciable quantity of chloride. Nitro-groups, and not the chlorine atoms, had evidently suffered replacement by amino-groups. The dark red solid, which dissolved completely in concentrated sulphuric acid, was precipitated on dilution as an orange powder, which seemed, however, to be a mixture of bases, for crystallisation from alcohol failed to produce a pure substance.

Summary.

(1) The monochlorination of 2-chloro-4-nitrotoluene with antimony trichloride or ferric chloride as catalyst leads to a mixture of isomerides, from which 2 : 6-dichloro-4-nitrotoluene crystallises out in a yield of more than 30 per cent. A method of separating the isomerides completely has not been devised, but probably the chief product is 2 : 6-dichloro-4-nitrotoluene.

(2) This result, when compared with the nitration of 2-chloro-4-nitrotoluene (Morgan and Drew, T., 1920, **117**, 793), in which more than 85 per cent. of the product is 2-chloro-4 : 5-dinitrotoluene, seems to show that either the nature of the entering group or the catalyst employed in the chlorination has a considerable effect on the position of substitution. It has not yet been possible to decide on the correct explanation.

The author is much indebted to Professor Lapworth, F.R.S., and to Dr. Hope for their interest in this investigation, and to Mr. Fred Hall for some assistance in the analytical portion of the work. His thanks are also due to the Ramsay Memorial Fellowship Trust for a Fellowship which has greatly facilitated this research.

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XCII.—*Constitution of Picrorocellin, a Diketopiperazine Derivative from* Roccella fuciformis.

By Martin Onslow Forster and William Bristow Saville.

In reviewing the vast number of chemical individuals which have been isolated from lichens, the absence of nitrogenous compounds is particularly noticeable. On this account a special interest attaches to picrorocellin, the colourless, crystalline, bitter substance obtained by Stenhouse and Groves (*Annalen*, 1877, **185**, 14) from *Roccella fuciformis* probably coming from the west coast of Africa, and giving indications of having grown on limestone rocks. At the death of Mr. C. E. Groves, the collection of chemical materials which he had assembled was presented to the Royal Institution by the Misses Groves; it included a specimen of picrorocellin, and by the kindness of Sir James Dewar, to whom our thanks are due, this has been entrusted to us for investigation.

Stenhouse and Groves ascribed to picrorocellin the empirical formula $C_{27}H_{29}O_5N_3$, and found that when heated with aqueous sodium hydroxide it is converted into a compound which they represented by the expression $C_{24}H_{25}O_3N_2$, ammonia being liberated. They also found that hot glacial acetic acid containing a small proportion of hydrochloric acid transforms the original substance into the pale yellow xanthorocellin, appearing to have the composition $C_{21}H_{17}O_2N_2$. Furthermore, they oxidised xanthorocellin with nitric acid, obtaining benzaldehyde and benzoic acid, together with a yellow substance which was stated not to be a nitrobenzoic acid, and a sparingly soluble, colourless compound which was not identified.

Whilst we confirm the foregoing results qualitatively, our own experiments have led us to different conclusions regarding the formulæ. This is probably due to the fact that Stenhouse and Groves dried their materials at 100° before analysis and, as will appear later, varying amounts of water and of methyl alcohol may have been thus removed from two of the compounds. The actual composition of picrorocellin is $C_{20}H_{22}O_4N_2$, whilst the substance obtainable by the action of aqueous sodium hydroxide, and produced more economically by heating picrorocellin at the melting point, has the composition $C_{20}H_{20}O_3N_2$; we therefore propose to call this compound *anhydropicrorocellin*. Xanthorocellin has the empirical formula $C_{19}H_{16}O_3N_2$, and is also produced by the more protracted heating of picrorocellin, which is thus decomposed in two stages involving the loss of water and of methyl alcohol, respec-

tively. This conclusion is confirmed by (1) the behaviour of dimethylpicrorocellin, $C_{22}H_{26}O_4N_2$, which contains two methoxyl groups as against one in picrorocellin, (2) the presence of a single methoxyl group in methylanhydropicrorocellin, and (3) the absence of methoxyl groups from xanthorocellin and methylxanthorocellin.

The oxidation of xanthorocellin with nitric acid yields benzaldehyde with benzoic and *p*-nitrobenzoic acids, the last-named having been overlooked because it forms with benzoic acid a molecular compound which obstinately defies ordinary methods of resolution into its components. The sparingly soluble, colourless compound noticed, but not identified by the previous investigators, has the empirical formula $C_5H_4O_4N_2$ and sublimes at 300°, when a portion decomposes; whilst resisting hot nitric acid, it is very readily hydrolysed by dilute sodium hydroxide, giving oxalic acid (2 mols.), ammonia (1 mol.), and methylamine (1 mol.). The absence of methyl alcohol, formaldehyde, and formic acid as products of this decomposition having been established, there does not appear to be any constitution alternative to that of 2 : 3 : 5 : 6-tetraketo-1-methylpiperazine (2 : 3 : 5 : 6-tetraketo-1-methylhexahydro-1 : 4-diazine),

(I.) CO·N(CH$_3$)·CO / CO—NH—CO   or   (II.) CO·N(CH$_3$)·CO / CO—N═C·OH ,

first obtained by Dubsky (*Ber.*, 1916, **49**, 1039; 1919, **52**, 216), and corresponding with the tetraketopiperazine described by de Mouilpied and Rule (T., 1907, **91**, 176; 1909, **95**, 549). This conclusion receives confirmation from the behaviour towards (1) aniline, which liberates ammonia, producing oxanilide and phenyloxamide, together with a third substance which may be unsymmetrical phenylmethyloxamide, and (2) phenylhydrazine, which yields oxalylphenylhydrazide. *Moreover, the corresponding oxidation product from methylxanthorocellin, having the empirical formula* $C_6H_6O_4N_2$, *is resolved by dilute aqueous sodium hydroxide into* oxalic acid (2 mols.) and methylamine (2 mols.), whilst aniline liberates methylamine and produces oxanilide with symmetrical phenylmethyloxamide; consequently, it appears to be 2 : 3 : 5 : 6-tetraketo-1 : 4-dimethylpiperazine, derived from I.

Thence it follows that the constitution of methylxanthorocellin is that of 2 : 5-diketo-3 : 6-dibenzylidene-1 : 4-dimethylpiperazine,

(III.) C$_6$H$_5$·CH:C—N(CH$_3$)·CO / CO·N(CH$_3$)·C:CH·C$_6$H$_5$,

a conclusion which we have now confirmed by synthesis, *for* 2 : 5-diketo-3 : 6-dibenzylidenepiperazine, the compound obtained by Sasaki (*Ber.*, 1921, **54**, [*B*], 163) on condensing diketopiperazine

(glycine anhydride) with benzaldehyde (2 mols.) yields a dimethyl derivative which we find to be identical with methylxanthorocellin. Consequently, xanthorocellin is 2 : 5-diketo-3 : 6-dibenzylidene-1-methylpiperazine,

$$\text{(IV.)}\quad \begin{array}{l} C_6H_5\cdot CH{:}\underset{|}{C}—N(CH_3)\cdot \underset{|}{C}O \\ \qquad\qquad\quad CO—NH—C{:}CH\cdot C_6H_5 \end{array},$$

which explains the production of benzaldehyde (2 mols.) and tetraketo-1-methylpiperazine on oxidation with nitric acid. The constitution of picrorocellin itself, however, remains uncertain regarding the position (1 or 4) of the *N*-methyl group in the formula

$$\text{(V.)}\quad \begin{array}{l} C_6H_5\cdot CH(O\cdot CH_3)\cdot \underset{|}{C}H\cdot N(CH_3)\cdot \underset{|}{C}O \\ \qquad\qquad\qquad\qquad\quad CO—NH—CH\cdot CH(OH)\cdot C_6H_5 \end{array},$$

which, in all other respects, explains the behaviour of the substance including its conversion into anhydropicrorocellin,

$$\text{(VI.)}\quad \begin{array}{l} C_6H_5\cdot CH(O\cdot CH_3)\cdot \underset{|}{C}H\cdot N(CH_3)\cdot \underset{|}{C}O \\ \qquad\qquad\qquad\qquad\quad CO—NH—C{:}CH\cdot C_6H_5 \end{array},$$

at the melting point.

These conclusions are further confirmed by the polarimetric evidence. Whilst xanthorocellin (IV) and methylxanthorocellin (III) are optically inactive, picrorocellin (V) with $[M]_D$ 44° approaches internal compensation, which is profoundly disturbed in anhydropicrorocellin (VI) with $[M]_D$ —1558° and in methyl-anhydropicrorocellin,

$$\text{(VII.)}\quad \begin{array}{l} C_6H_5\cdot CH(O\cdot CH_3)\cdot \underset{|}{C}H\cdot N(CH_3)\cdot \underset{|}{C}O \\ \qquad\qquad\qquad\qquad\quad CO\cdot N(CH_3)\cdot C{:}CH\cdot C_6H_5 \end{array},$$

with $[M]_D$ —2314°, because in both compounds it will be seen that, of the four asymmetric carbon atoms originally present in picrorocellin, the two which have been suppressed are both situated on one side of the plane traversing the carbonyl groups. On the other hand, it is clear that in dimethylpicrorocellin,

$$\text{(VIII.)}\quad \begin{array}{l} C_6H_5\cdot CH(O\cdot CH_3)\cdot \underset{|}{C}H\cdot N(CH_3)\cdot \underset{|}{C}O \\ \qquad\qquad\qquad\qquad\quad CO\cdot N(CH_3)\cdot CH\cdot CH(O\cdot CH_3)\cdot C_6H_5 \end{array},$$

there is a plane of symmetry passing through the carbonyl groups, and therefore the condition of internal compensation prevails although four carbon atoms are asymmetric; this is confirmed by its optical inactivity.

Reviewing these experiments, it seems probable that picrorocellin is developed in the lichen by inter-molecular condensation of the two α-amino-acids, α-methylamino-β-methoxy-β-phenylpropionic, $C_6H_5\cdot CH(O\cdot CH_3)\cdot CH(NH\cdot CH_3)\cdot CO_2H$, and α-amino-β-hydroxy-β-phenylpropionic acid, $C_6H_5\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2H$, or

of the corresponding acids in which the *N*-methyl group is transposed. With the object of testing this conclusion, and simultaneously deciding the position of the doubtful *N*-methyl group, we propose to attempt the synthesis of picrorocellin on the lines indicated.

At one time it was hoped that the point might be ascertained from the product of oxidising anhydropicrorocellin (VI). Having found that the methyl derivative (VII) is oxidised in acetone by potassium permanganate to benzaldehyde and 2 : 3 : 5-triketo-6-α-methoxybenzyl-1 : 4-dimethylpiperazine,

$$\text{(IX.)}\quad \begin{array}{l} C_6H_5{\cdot}CH(O{\cdot}CH_3){\cdot}CH{\cdot}N(CH_3){\cdot}CO \\ \qquad\qquad\qquad\qquad\quad CO{\cdot}N(CH_3){\cdot}CO \end{array},$$

it was expected that hydrolysis of this compound would yield oxalic acid, methylamine, and α-methylamino-β-methoxy-β-phenylpropionic acid. Had this happened, the corresponding procedure with anhydropicrorocellin (VI) should have given either the above amino-acid, or α-amino-β-methoxy-β-phenylpropionic acid, thus determining the position of the *N*-methyl group; but, unfortunately, the only aromatic product of hydrolysis is, in both cases, phenylpyruvic acid. This must be due to removal of methyl alcohol, transforming the triketopiperazines into acyl derivatives of α-aminocinnamic acid; it has been observed on previous occasions (E. Erlenmeyer, jun., *Ber.*, 1897, **30**, 2976; Ruhemann and Stapleton, T., 1900, **77**, 246) that such compounds are resolved by hydrolysis into phenylpyruvic acid, and thus α-aminocinnamic acid has hitherto escaped isolation.

In conclusion, it is noteworthy that although W. Brieger's compendium of lichen products, recently appearing in the "Handbuch der biologischen Arbeitsmethoden" (E. Abderhalden), embraces 135 compounds to which empirical formulæ have been ascribed, picrorocellin remains, as it was in 1877, the only one which contains nitrogen.

Experimental.

Picrorocellin, $C_{20}H_{22}O_4N_2$ (V).

The better of two specimens in Mr. Groves's collection was recrystallised from boiling alcohol, 5 grams requiring 60 c.c., and separating in massive, transparent, rectangular prisms melting between 190° and 220°, according to the rate of heating, the melting point recorded by Stenhouse and Groves being 192—194° (Found: C = 67·9, 67·5; H = 6·3, 6·3; N = 8·0, 7·9; $CH_3{\cdot}O$ = 8·8, 8·9. $C_{20}H_{22}O_4N_2$ requires C = 67·8; H = 6·2; N = 7·9; $1CH_3{\cdot}O$ = 8·7 per cent.). Picrorocellin is insoluble in cold, dilute aqueous acids or alkalis, and resists the action of potassium permanganate in boiling acetone; it remains unaltered when heated in aqueous

alcohol with hydroxylamine or phenylhydrazine acetate. A solution containing 0·9991 gram in chloroform diluted to 25 c.c. gave α_D 0° 30′ in a 1-dcm. tube, whence $[\alpha]_D$ 12·5°, corresponding with $[M]_D$ 44·3°.

The second specimen, containing also colouring matters, fat, and another nitrogenous compound, was treated three times with boiling benzene to extract the major portion of the colouring matters and fat. The residue was powdered, and in quantities of 25 grams treated with a mixture of alcohol (75 c.c.) and 10 per cent. aqueous sodium hydroxide (75 c.c.), which dissolved the picrorocellin; this was precipitated from the filtrate by acetic acid diluted with an equal volume of alcohol. Repetition of this process gave a product which required only one recrystallisation from boiling alcohol.

Dimethylpicrorocellin, $C_{22}H_{26}O_4N_2$ (VIII).—Ten grams of picrorocellin dissolved in a mixture of 10 per cent. aqueous sodium hydroxide (30 c.c.) and alcohol (30 c.c.) were agitated with excess of methyl sulphate, when the dimethyl derivative rapidly separated in quantitative yield as a colourless solid moderately soluble in boiling alcohol, from which it crystallised in lustrous, transparent, elongated prisms melting at 229° (Found: C = 69·2, 69·1; H = 6·7, 6·8; N = 7·6, 7·4; CH_3·O = 15·5, 15·7. $C_{22}H_{26}O_4N_2$ requires C = 69·1; H = 6·8; N = 7·3; $2CH_3$·O = 16·2 per cent.). The substance is insoluble in cold, dilute aqueous acids or alkalis, and does not combine with hydroxylamine or phenylhydrazine; it is optically inactive.

Reduction of Dimethylpicrorocellin.—After estimating the methoxyl content by the Zeisel method (at 140°), it was noticed that a solid remained suspended in the hydriodic acid (*d* 1·26); this was filtered and extracted with aqueous potassium iodide, which diminished the colour from bluish-black to pale brown, recrystallisation from boiling water giving minute, lustrous, colourless plates melting at 165° (Found: C = 74·7, 74·5; H = 6·7, 6·7; N = 8·8. $C_{20}H_{22}O_2N_2$ requires C = 74·5; H = 6·8; N = 8·7 per cent.). The substance is insoluble in dilute, aqueous acids or alkalis, and does not yield ammonia with boiling 10 per cent. aqueous sodium hydroxide. It dissolves in concentrated nitric or sulphuric acid without change, and it does not combine with phenylhydrazine. It is to be regarded as 2 : 5-diketo-3 : 6-dibenzyl-1 : 4-dimethylpiperazine,

(X.) C_6H_5·CH_2·CH·N(CH_3)·CO
CO·N(CH_3)·CH·CH_2·C_6H_5 ,

being subsequently identified with the product of reducing (see below) the dimethyl derivative of Sasaki's 2 : 5-diketo-3 : 6-dibenzylidenepiperazine.

Anhydropicrorocellin, $C_{20}H_{20}O_3N_2$ (VI).—Picrorocellin was treated with about 10 parts of boiling, aqueous sodium hydroxide (10 per cent.) until the liberation of ammonia ceased and a clear solution was produced. The solid substance precipitated by dilute sulphuric acid was triturated with a solution of sodium carbonate and recrystallised, first from alcohol and then from benzene to which light petroleum was added, separating in needles which melt at 155° (Found : C = 71·2; H = 5·8; N = 8·4; CH_3·O = 9·0. $C_{20}H_{20}O_3N_2$ requires C = 71·4; H = 5·9; N = 8·3; 1CH_3·O = 9·2 per cent.). A less wasteful, but more tedious, method of preparation consists in melting picrorocellin in quantities not exceeding 5 grams, and then maintaining the temperature at 180° during five to ten minutes, aqueous vapour being briskly evolved; the colour becomes deep amber and the product, on cooling, sets to a transparent resin in which crystals are embedded and which dissolves slowly in 10 per cent. aqueous sodium hydroxide. The precipitate formed by acetic acid was boiled with 50 per cent. alcohol, which left a small proportion of xanthorocellin undissolved, the anhydropicrorocellin crystallising from the filtrate. A solution containing 1·0135 grams in chloroform diluted to 25 c.c. gave α_D − 18° 48′ in a 1-dcm. tube, whence $[\alpha]_D$ −463·7°, corresponding with $[M]_D$ −1558°.

Methylanhydropicrorocellin, produced by methyl sulphate from a solution of anhydropicrorocellin in aqueous sodium hydroxide, was crystallised from alcohol followed by benzene to which light petroleum was added, and separated in colourless prisms melting at 139° (Found : C = 72·3, 72·3; H = 6·1, 6·2; N = 8·1; CH_3·O = 8·8, 8·8. $C_{21}H_{22}O_3N_2$ requires C = 72·0; H = 6·3; N = 8·0; 1CH_3·O = 8·9 per cent.). A solution containing 0·4991 gram in chloroform diluted to 25 c.c. gave α_D −13° 12′ in a 1-dcm. tube, whence $[\alpha]_D$ −661·2°, corresponding with $[M]_D$ −2314°.

Xanthorocellin (2 : 5-*Diketo*-3 : 6-*dibenzylidene*-1-*methylpiperazine*), $C_{19}H_{16}O_2N_2$ (IV).

As already stated, xanthorocellin is produced by heating picrorocellin beyond the stage at which anhydropicrorocellin is formed, but the more convenient method is that described by Stenhouse and Groves (*loc. cit.*), who added a few drops of hydrochloric acid to a solution of picrorocellin in hot, glacial acetic acid, when a yellow colour was immediately developed; after being boiled during fifteen minutes, the liquid was poured into a large volume of alcohol, and the felted mass of silky threads recrystallised from boiling alcohol, by which the substance is dissolved very sparingly, separating in long, faintly yellow, slender needles melting at 184° (Found : C = 75·2; H = 5·1; N = 9·2; CH_3·N = 9·0. $C_{19}H_{16}O_2N_2$ re-

quires C = 75·0; H = 5·3; N = 9·3; CH_3·N = 9·5 per cent.). The substance does not contain a methoxyl group and is optically inactive. Although insoluble in cold, dilute, aqueous acids and alkalis, it forms a deep yellow solution in a mixture of 10 per cent. aqueous sodium hydroxide and alcohol; moreover, the substance freshly precipitated from such solutions will dissolve in aqueous alkali hydroxides. It is not benzoylated by the Schotten-Baumann process, and does not combine with hydroxylamine or phenylhydrazine.

Methylxanthorocellin (2 : 5-*Diketo*-3 : 6-*dibenzylidene*-1 : 4-*dimethylpiperazine*) was prepared by heating dimethylpicrorocellin (2 grams) with acetic anhydride (15 c.c.) during four hours under reflux, the yellow solution being then poured into a large volume of water. The pale yellow prisms obtained on adding water to a solution of the solid product in alcohol evidently contained solvent of crystallisation, showing signs of fusion on approaching 90°, resolidifying soon after 100°, and finally melting below 140°. On removing this at 100° and recrystallising from light petroleum, the substance separated in slender, very faintly yellow needles melting at 143°. When prepared by the process which converts picrorocellin into xanthorocellin, the product is usually sticky, and although quite suitable for oxidation to tetraketodimethylpiperazine (see below), the separation of methylxanthorocellin, which is probably contaminated with methylanhydropicrorocellin, becomes difficult and wasteful (Found: C = 75·6, 75·5; H = 5·6, 5·5; N = 8·8. $C_{20}H_{18}O_2N_2$ requires C = 75·5; H = 5·7; N = 8·8 per cent.). The substance does not contain a methoxyl group and is optically inactive; it displays remarkable dimorphism, the above-mentioned needles, which attain half an inch in length, changing during twenty-four hours into pale yellow, transparent, rhomboidal prisms melting at the temperature stated. It was subsequently identified with the product of methylating (see below) Sasaki's 2 : 5-diketo-3 : 6-dibenzylidenepiperazine.

Oxidation Experiments.

Xanthorocellin.—Five grams were dissolved in 10 c.c. of boiling glacial acetic acid and allowed to cool slowly, the cold liquid thus remaining free from crystals; 5 c.c. of concentrated nitric acid having been added, there ensued on gentle heating a very vigorous action which required control by cooling at intervals. Meanwhile, slender, colourless crystals rapidly separated, and when action had been completed on the water-bath the liquid set to a semi-solid paste on cooling. Thirty c.c. of alcohol having been added, the solid (1·65 grams) was filtered, washed three times with small

quantities of alcohol, and recrystallised from boiling, glacial acetic acid, which deposited minute, lustrous, transparent, rectangular plates (Found: C = 38·6; H = 2·5; N = 18·1; CH_3·N = 16·9, 17·0. $C_5H_4O_4N_2$ requires C = 38·5; H = 2·6; N = 17·9; CH_3·N= 18·6 per cent.). The substance dissolves readily in boiling water and separates in minute, transparent, four-sided prisms. It has not a definite melting point, becoming brown at about 280° and in part subliming, in part decomposing, at 300°. Although differing somewhat in this respect from tetraketomethylpiperazine as prepared from oxalyl chloride and methyloxamide by Dubsky (*loc. cit.*), whose product is described as beginning to decompose at 260°, the behaviour on hydrolysis (see below) points unmistakably to that substance having the constitution I or II.

The filtrate and washings from the foregoing compound were subjected to a current of steam, the alcohol being followed by benzaldehyde which was converted into the phenylhydrazone (0·8 gram). The aqueous residue yielded a pale yellow, crystalline solid (2·3 grams) on cooling, and it was only after accumulating this product from a larger quantity of xanthorocellin that its identity was established. The difficulty arose from the fact, which does not appear to have been recorded, that benzoic and *p*-nitrobenzoic acids form a compound, in the molecular proportion 2 : 1, crystallising from light petroleum and melting indefinitely at 182—198°. The material obtained from xanthorocellin was recrystallised from boiling water and the product, melting at 192—208°, treated with slight excess of barium carbonate suspended in a moderate amount of boiling water, the barium salt which crystallised from the filtrate on cooling being that of *p*-nitrobenzoic acid. On acidifying the filtrate from barium *p*-nitrobenzoate and recrystallising the precipitate from water, in which it dissolves much more readily than *p*-nitrobenzoic acid, the product melted at 174—184° and, after crystallisation from light petroleum, at 182—198° (Found: C = 61·7; H = 4·1; N = 3·4. $C_6H_4(NO_2)$·CO_2H requires C = 50·3; H = 2·9; N = 8·4. $2C_6H_5$·$CO_2H,C_6H_4(NO_2)$·CO_2H requires C = 61·3; H = 4·1; N = 3·4 per cent.). Moreover, by mixing benzoic and *p*-nitrobenzoic acids in the proportions indicated, and crystallising the product from the solvents mentioned, an exactly similar material was obtained, thus recalling the observation of Salkowski (*Ber.*, 1876, **9**, 24) that when a mixture of the two acids (1 : 1) is neutralised with barium carbonate, a salt having the composition C_6H_5·CO_2·Ba·CO_2·C_6H_4·NO_2 is produced.

Methylxanthorocellin.—Proceeding as in the case of xanthorocellin, colourless crystals rapidly separated from the mixed nitric and acetic acids; these having been treated in the same way were

deposited in minute, lustrous, transparent, rhomboidal plates from hot glacial acetic acid (Found: C = 42·5; H = 3·5; N = 16·3. $C_6H_6O_4N_2$ requires C = 42·4; H = 3·5; N = 16·5 per cent.). From the behaviour on hydrolysis and with hot aniline (see below) the substance must be regarded as 2 : 3 : 5 : 6-*tetraketo*-1 : 4-*dimethylpiperazine*, $\begin{matrix}CO{\cdot}N(CH_3){\cdot}CO\\ | \qquad\qquad |\\ CO{\cdot}N(CH_3){\cdot}CO\end{matrix}$. It is even more resistant to rise of temperature than the monomethyl compound, beginning to darken at about 340°, when a sublimate collects, and undergoing general decomposition at about 360°.

Anhydropicrorocellin.—A solution containing 1 gram in 50 c.c. of cold acetone required about the same weight of finely powdered potassium permanganate to produce a permanent coloration, but the final stage was not definite. On reducing with sulphurous acid the manganese precipitate suspended in water, there remained a white solid which crystallised from boiling water in lustrous, transparent, six-sided prisms melting at 206° (Found: C = 59·7; H = 5·2; N = 10·9; $CH_3{\cdot}O$ = 11·6. $C_{13}H_{14}O_4N_2$ requires C = 59·5; H = 5·3; N = 10·7; $1CH_3{\cdot}O$ = 11·8 per cent.). Thus it is to be regarded as 2 : 3 : 5-*triketo*-6-α-*methoxybenzyl*-1(or 4)-*methylpiperazine*; a solution containing 1·0067 grams in chloroform diluted to 25 c.c. gave α_D 0° 45′ in a 1-dcm. tube, whence $[\alpha]_D$ 18·6°, corresponding with $[M]_D$ 48·7°. On evaporating the acetone there remained crystals suspended in benzaldehyde, and the latter having been allowed to undergo oxidation in air, aqueous sodium carbonate left undissolved a small quantity of unchanged anhydropicrorocellin.

Methylanhydropicrorocellin.—A solution containing 1 gram in 50 c.c. of cold acetone remained permanently pink when the same weight of finely powdered potassium permanganate had been added, the filtrate depositing 0·6 gram of colourless crystals on evaporation. Light petroleum added to a solution of the substance in benzene caused the separation of needles in spherical aggregates, or in transparent, rhomboidal plates when crystallisation was tardy (Found: C = 61·0; H = 5·6; N = 10·4; $CH_3{\cdot}O$ = 10·9. $C_{14}H_{16}O_4N_2$ requires C = 60·9; H = 5·8; N = 10·2; $1CH_3{\cdot}O$ = 11·2 per cent.). It melts at 176°, and is to be regarded as 2 : 3 : 5-*triketo*-6-α-*methoxybenzyl*-1 : 4-*dimethylpiperazine* (IX); a solution containing 0·4002 gram in chloroform diluted to 25 c.c. gave α_D −0° 15′ in a 1-dcm. tube, whence $[\alpha]_D$ −15·6°, corresponding with $[M]_D$ −43·0°. The precipitate from which the acetone solution was filtered having been suspended in water and reduced with sulphurous acid, benzoic acid separated from the liquid.

Transformations of the Ketopiperazines.

Hydrolysis of Tetraketomethylpiperazine.—Whilst readily soluble in dilute, aqueous sodium hydroxide or carbonate, it is not reprecipitated by acids, and hydrolysis indicated by liberation of ammonia rapidly becomes discernible. On distilling the solution in aqueous sodium hydroxide, collecting the ammonia and methylamine in standardised hydrochloric acid, adding sulphuric acid to the liquid remaining in the flask, and titrating this with potassium permanganate, the basic equivalent and the liberated oxalic acid were estimated in one operation (Found: $C_2O_2 = 71{\cdot}1$; $N = 18{\cdot}0$. $C_5H_4O_4N_2$ requires $2C_2O_2 = 71{\cdot}8$; $N = 17{\cdot}9$ per cent.). Although this result was confirmed by an estimation of the oxalic acid as calcium oxalate, it seemed advisable to examine the distillate for methyl alcohol and formaldehyde, whilst a search for formic acid was made in the residual liquid. A solution of the substance containing 1 gram in aqueous sodium hydroxide was therefore distilled into dilute sulphuric acid, a portion (5 c.c.) of the distillate being found to remain colourless after five minutes' heating on the water-bath with peptone (0·8 gram), hydrochloric acid (5 c.c.), and ferric chloride (3 drops of a 10 per cent. solution); a negative result also followed the application of this test to the distillate after treatment with potassium permanganate, and the residual liquid, having been freed from oxalic acid, did not reduce mercuric chloride. It was necessary to apply these tests because we were long in doubt regarding the condition of one carbon atom; determinations of *N*-methyl were persistently too low, probably because of the high temperature resisted by the substance.

Action of Aniline on Tetraketomethylpiperazine.—According to de Mouilpied and Rule (*loc. cit.*), tetraketopiperazine itself yields an anilide, and this behaviour delayed our recognition of the compound $C_5H_4O_4N_2$ as its methyl derivative, because the substance is rapidly converted into oxanilide, phenyloxamide, and a compound isomeric with phenylmethyloxamide, but melting at 174°. Two grams were heated with 15 grams of boiling aniline during three hours under reflux, the crystals which separated during the next twelve hours being filtered and washed with 5 c.c. of aniline and 10 c.c. of alcohol. The product (4 grams) was extracted six times with boiling water, which left oxanilide (2 grams) undissolved and deposited crystals on cooling. The aniline-alcohol liquor having been subjected to a current of steam, the filtered residual solution gave crystals which were then associated with those separated from the oxanilide and extracted with benzene; this deposited minute, pale yellow needles melting at 174°, and left phenyloxamide (m. p.

226°) undissolved, identity being established by analysis and the melting point of a mixture with the actual substance. In view of the copious evolution of ammonia during the action, we suspect the compound melting at 174° to be unsymmetrical phenylmethyloxamide (Found: C = 60·9; H = 5·4; N = 15·9. $C_9H_{10}O_2N_2$ requires C = 60·7; H = 5·6; N = 15·7 per cent.). It has not yet been possible to confirm this, because the substance does not appear to have been prepared, and an attempt to produce it by heating oxamethane with methylaniline took another course, yielding tetraketopiperazine; but it is not symmetrical phenylmethyloxamide (m. p. 187°), a mixture with that compound beginning to shrink at 172° and becoming completely fused at 180°.

Hydrolysis of Tetraketodimethylpiperazine.—Although not soluble in aqueous sodium carbonate, the dimethyl derivative is rapidly dissolved by the hydroxide, and is completely hydrolysed to methylamine (2 mols.) and oxalic acid (2 mols.) on heating the liquid (Found: C_2O_2 = 65·1; N = 16·4. $C_6H_6O_4N_2$ requires $2C_2O_2$ = 65·9; N = 16·5 per cent.).

Action of Aniline on Tetraketodimethylpiperazine.—Proceeding as in the foregoing case, oxanilide separated from the aniline on cooling, whilst the more soluble product was found to be symmetrical phenylmethyloxamide, melting at 187° (Found: C = 60·7; H = 5·4; N = 15·6. $C_9H_{10}O_2N_2$ requires C = 60·7; H = 5·6; N = 15·7 per cent.) and not depressing the melting point of that substance when mixed with it.

Hydrolysis of 2 : 3 : 5-Triketo-6-α-methoxybenzyl-1(or 4)-methylpiperazine (m. p. 206°).—Two grams were heated on the water-bath with 10 per cent. aqueous sodium hydroxide (40 c.c.) during one and a half hours, sodium oxalate separating in slender needles which changed to transparent prisms, and methylamine being liberated. The filtrate giving scarcely any precipitate with acetic acid was saturated with salt and extracted with ether, which deposited a small quantity of oily matter giving a green coloration with ferric chloride. A voluminous precipitate then appeared in the salt solution, and after recrystallisation from boiling alcohol containing a little water was found to be sodium phenylpyruvate, from which the phenylhydrazone melted at 160° (Found: N = 11·1. $C_{15}H_{14}O_2N_2$ requires N = 11·0 per cent.). An attempt to identify, by heating with ammonia, the α-amino-acid from which the triketopiperazine is derived also failed, the substance being recovered unchanged.

Hydrolysis of 2 : 3 : 5-Triketo-6-α-methoxybenzyl-1 : 4-dimethylpiperazine (m. p. 176°).—Two grams were heated on the water-bath with 10 per cent. aqueous sodium hydroxide (30 c.c.) during

two hours, sodium oxalate separating and methylamine being liberated. On acidifying the filtrate with dilute sulphuric acid, the precipitate consisted of phenylpyruvic acid and melted, after crystallisation from benzene and light petroleum, at 154°, also developing the characteristic deep green coloration with ferric chloride (Found: C = 65·9; H = 4·9. $C_9H_8O_3$ requires C = 65·9; H = 4·9 per cent.).

Methylation of 2 : 5-*Diketo*-3 : 6-*dibenzylidenepiperazine.*—The piperazine derivative was prepared by condensing diketopiperazine (glycine anhydride) with benzaldehyde (Sasaki, *loc. cit.*), and the solution in equal parts of alcohol and aqueous sodium hydroxide (10 per cent.) was treated with methyl sulphate. The product having been crystallised from light petroleum melted at 143°, and was found to be identical, in all respects including dimorphism, with methylxanthorocellin.

Reduction of 2 : 5-*Diketo*-3 : 6-*dibenzylidene*-1 : 4-*dimethylpiperazine.*—The synthetic methylxanthorocellin, prepared as above, was reduced with hydriodic acid (*d* 1·26) at 140°, the suspended solid being washed and extracted with aqueous potassium iodide. After recrystallisation from boiling water, it melted at 165°, and was found to be identical with the product from dimethylpicrorocellin.

The foregoing experiments were made in the Davy-Faraday Laboratory of the Royal Institution.

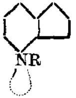
ROYAL INSTITUTION, W.1. [*Received, April 6th,* 1922.]

XCIII.—*Polynuclear Heterocyclic Aromatic Types. Part I. Some Indenoquinoline Derivatives.*

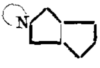
By JAMES WILSON ARMIT and ROBERT ROBINSON.

THE application of the theory of partial valency to benzenoid substances (Robinson and Robinson, T., 1917, **111**, 964; 1918, **113**, 640; Perkin and Robinson, *ibid.*, 1919, **115**, 943; Robinson, *Mem. Manchester Phil. Soc.*, 1920, **64**, 4; *J. Soc. Dyers and Col.*, 1921, **37**, 77; Kermack, Perkin, and Robinson, T., 1921, **119**, 1607; Kermack and Robinson, this vol., p. 437) leads to the conclusion that many aromatic types as yet unknown should be capable of existence, and in the present series of investigations it is proposed to survey the field of the heterocyclic substances from this point of view and with the particular object of throwing light on the conditions underlying the manifestation of the phenomenon of cyclic conjugation. At the present time, authentic derivatives of pentamethine, $(CH)_5$, the lower ring homologue of benzene, are

unknown, and there is reason to believe that this substance itself is incapable of separate existence (compare Kermack and Robinson, *loc. cit.*), but, on the other hand, theoretical considerations indicate that in fusion with other ring systems such a nucleus might occur and, for example, in the forms :

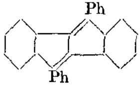
(I.) 

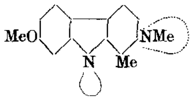
(II.)



(III.)

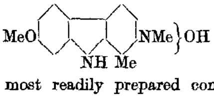
It should be noted that the hydrocarbon, $C_{28}H_{18}$, obtained by the action of magnesium phenyl bromide on diphensuccindandione (Brand and Ludwig, *Ber.*, 1920, **53**, [*B*], 809) may be a representative of type II, but its brown colour and behaviour on oxidation are in better accord with the intra-annular quinonoid formula IV.

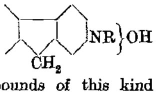
(IV.) 



(V.)

The unusual non-basic six-membered and basic five-membered rings in I and III occur together in methylharmine (Perkin and Robinson, *loc. cit.*), which is obtained by the dehydration of harmine methohydroxide (VI), and it was therefore thought possible that a substance derived from pentamethine might be produced from a quaternary hydroxide containing the group VII or an analogous structure.

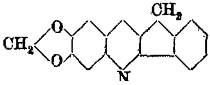
(VI.) 



(VII.)

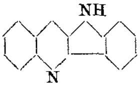
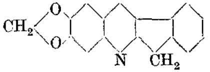
The most readily prepared compounds of this kind are the methohydroxides derived from indenoquinolines, and accordingly these were chosen for examination in the first place. The condensation of aminopiperonal (Rilliet and Kreitmann, *Helv. Chim. Acta*, 1921, 4, 588) and α-hydrindone in cold alcoholic solution in presence of potassium hydroxide gave an unexpected result, since the product was the unsaturated ketone (VIII), a bright red, crystalline substance which was changed to the quinoline derivative (IX) on boiling with acetic acid.

(VIII.)

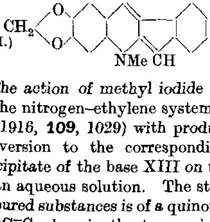
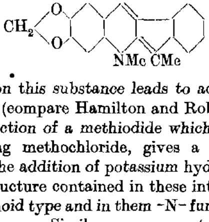


(IX.)

The decomposition of the methosulphate of this base with alkali in aqueous solution resulted in the production of a green precipitate of ambiguous composition, and an anhydro-base could not be isolated. This result is not surprising in view of the further observation that the metho-salts of quindoline (X), which is constitutionally related not only to the substance IX but, in addition, to harmine, also gave anomalous results on treatment with alkali. It is proposed to extend the investigation to analogous bases not containing benzene nuclei, but the preparation of these is a matter of considerable difficulty. Aminopiperonal condenses normally with β-hydrindone and the indenoquinoline (XI) is directly obtained.

(X.)   (XI.)

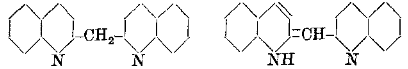
The methosulphate of this base on treatment with aqueous alkali yields a deep purple, crystalline anhydro-base, $C_{18}H_{13}O_2N$, which is reconverted by acids to the metho-salts of XI. On account of its remarkable colour this substance cannot well be regarded as of full cyclic conjugated type and the constitution XII is assigned to it.

(XII.)   (XIII.)

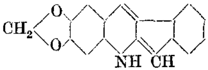
The action of methyl iodide on this substance leads to addition to the nitrogen–ethylene system (compare Hamilton and Robinson, T., 1916, **109**, 1029) *with production of a methiodide which, after* conversion to the corresponding methochloride, gives a purple precipitate of the base XIII on the addition of potassium hydroxide to an aqueous solution. The structure contained in these intensely coloured substances is of a quinonoid type and in them –N– functions as –C=C– does in the true quinones. Similar arrangements (both *o-* and *p-*) occur in the cyanines and in many other substances (compare Decker, *Ber.*, 1905, **38**, 2493), and might be termed "*azonoid,*" * the true benzenoid character being then distinguished as "*azenoid.*" An interesting example of azenoid–azonoid tau-

* Still more complex structures of quinonoid type are contained in the cyanine dyes derived from benzothiazoles which have recently been examined by Mills (this vol., p. 455). In these substances, not only does –N– replace the crossed double bond of a quinone, but in addition –S– replaces an ethylene linkage of the aromatic ring. *The type is "thiazonoid" and the further* theoretical possibilities are denoted by the terms "*oxonoid*" (*o-* and *p-*), "*thionoid*" (*o-* and *p-*), "*dioxonoid,*" "*diazonoid,*" "*dithionoid,*" "*thioxonoid,*" and "*oxazonoid.*"

tomerism has recently been observed in the case of diquinolylmethane (Scheibe and Rossner, *Ber.*, 1921, **54**, [*B*], 451), which occurs in colourless azenoid (XIV) and red azonoid (XV) modifications, the former being the more stable of the two.

(XIV.)  (XV.)

We believe that the indenoquinoline (XI) exhibits an analogous phenomenon, and can occur, under appropriate conditions, in the azonoid form XVI.

(XVI.) 

When the base is covered with a little glacial acetic acid, the crystals become pale brownish-violet and the solution dull mauve-red. On heating, an intense brownish-red solution is obtained and this becomes brownish-purple and more intensely coloured on cooling. The addition of a mineral acid at once produces a yellow, fluorescent solution. With formic acid, the cold solution is orange-yellow and the hot solution brownish-red, resembling that in acetic acid. This behaviour is plainly due to the stronger acidity of formic as compared with acetic acid and to the formate dissociating to some extent at an elevated temperature. The equilibrium in acetic acid is, we imagine, represented by the scheme :

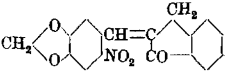
$$\text{XI} + C_2H_4O_2 \rightleftarrows \text{Indenoquinoline acetate} \rightleftarrows \text{XVI} + C_2H_4O_2.$$

The solution of the base in phenol is yellow and non-fluorescent, and this shows that a salt is not produced.

Colorations similar to those described above were not observed in analogous experiments with the isomeric indenoquinoline (IX). An account is also included of some indole derivatives derived from α- and β-hydrindones. Attempts are in progress to oxidise these to bases containing the grouping typified in the expression III.

EXPERIMENTAL.

6'-Nitro-3' : 4'-methylenedioxy-2-benzylidene-1-hydrindone,

 .

A moderately rapid stream of dry hydrogen chloride was passed into a solution of α-hydrindone (13·2 grams) and nitropiperonal

(19·5 grams) in glacial acetic acid (250 c.c.) during one and a half hours. On allowing to remain over-night, the condensation product separated in yellow, hexagonal prisms. It was collected and hydrogen chloride again passed through the filtrate, when a further crop was obtained, and this process was repeated until no more crystals appeared on standing. The total yield amounted to 60 per cent. of the theory. The substance is sparingly soluble in hot alcohol and is best recrystallised from acetic acid (Found : C = 65·9; H = 3·7; N = 4·7. $C_{17}H_{11}O_5N$ requires C = 66·0; H = 3·5; N = 4·5 per cent.). This compound melts at 182° and dissolves in sulphuric acid to a bright orange-red solution.

Attempts were made to produce the substance by the nitration under various conditions of piperonylidenehydrindone, but this process was found to be unsuitable. The following is a typical experiment. Piperonylidenehydrindone (from 13 grams of α-hydrindone) was ground in a mortar with nitric acid (200 c.c.; *d* 1·42). The substance partly dissolved to a blood-red solution, and before the whole had reacted the nitro-derivative separated in bright yellow crystals. The trituration was continued until red specks were no longer visible and the liquid had become pale orange-yellow. Water was then added and the precipitate collected. The substance crystallised from acetic acid in yellow, hexagonal prisms and also in needles and exhibited a definite melting point at 167° not altered by recrystallisation (Found : C = 59·0; H = 3·2; N = 7·4. A mixture of 84 per cent. of dinitro-derivative and 16 per cent. of mononitro-derivative requires C = 59·0; H = 3·0; N = 7·4 per cent.).

In view of this result, it is curious that prolonged treatment even with fuming nitric acid (*d* 1·5) did not effect any further nitration, and it seems probable that the second nitroxyl is introduced at an early stage in the process described and when the molecule is in a reactive condition. Thus the piperonylidenehydrindone doubtless undergoes a change in constitution when it forms the red halochromic solution in strong acids, and it is probably in this state that the substance can be dinitrated.

6′-*Amino*-3′ : 4′-*methylenedioxy*-2-*benzylidene*-1-*hydrindone* (VIII).

6-Aminopiperonal (8·3 grams) and α-hydrindone (6·7 grams) were dissolved in ethyl alcohol (120 c.c.) and an aqueous solution of potassium hydroxide (15 c.c. of 33 per cent.) was added with stirring. A scarlet, crystalline substance separated in a few minutes and filled the liquid. The precipitate was collected, washed, and dried, the yield amounting to 60 per cent. of that theoretically possible. This substance crystallises from alcohol, in which it is moderately

readily soluble, in long, deep red needles melting at 227—228° (Found: C = 72·7; H = 4·8; N = 5·2. $C_{17}H_{13}O_3N$ requires C = 73·1; H = 4·7; N = 5·0 per cent.).

This derivative may also be obtained, although not conveniently, by the reduction of nitropiperonylidenehydrindone with sodium sulphide. *It is sparingly soluble in benzene or ether, and can be diazotised and coupled with β-naphthol to a crimson azo-compound.*

6 : 7-*Methylenedioxy*-2 : 3-*indeno*(1 : 2)-*quinoline* (IX).

(*A*) Aminopiperonylidene-1-hydrindone was found to be quickly and completely converted into this quinoline derivative on boiling with glacial acetic acid. The diluted solution was basified by the addition of excess of potassium hydroxide and the precipitated base collected and crystallised from benzene. It separated in pale yellow needles or in hexagonal prisms, according as the solution was cooled quickly or slowly, and it may be obtained in a colourless form by recrystallisation from alcohol with the aid of animal charcoal (Found: C = 77·9; H = 4·0; N = 5·5. $C_{17}H_{11}O_2N$ requires C = 78·2; H = 4·2; N = 5·4 per cent.).

(*B*) Nitropiperonylidene-1-hydrindone (6·7 grams) was dissolved in boiling acetic acid (120 c.c.) and reduced by the gradual addition of zinc dust (20 grams). The solution became reddish-brown and then yellow, and when no further change of colour occurred a little animal charcoal was added and the mixture filtered hot. The filtrate was diluted with water (250 c.c.), and a voluminous, chalky, yellow precipitate of a hydrochloride thrown down by the addition of concentrated hydrochloric acid (40 c.c.). This was collected and the free base obtained by decomposition of the salt in methyl-alcoholic solution with ammonia. The substance was then crystallised from benzene and obtained in pale yellow needles melting at 186°, alone or mixed with the specimen produced as described above (*A*). The yield was 3 grams, which is 53 per cent. of that theoretically possible.

Dilute acid solutions of this indenoquinoline exhibit bright blue fluorescence. The base is readily soluble in acetic acid and is not precipitated on dilution with water. It forms a *hydrochloride* which is moderately soluble in water, but very sparingly soluble in dilute hydrochloric acid or sodium chloride solutions. It crystallises from hot water containing a little hydrochloric acid in pale yellow needles which begin to decompose at 260°. The *mercurichloride* is an extremely sparingly soluble derivative which crystallises from very dilute solution in pale yellow needles. Sparingly soluble salts are also obtained by the addition of nitric, oxalic, and picric acids to a dilute solution of the acetate.

Methosulphate.—This derivative was obtained in a yield of 75 per cent. of the theory by the interaction of the base with an excess of neutral methyl sulphate in boiling benzene. The salt separated from the solution and was recrystallised from a mixture of methyl and ethyl alcohols. It is readily soluble in the former, more sparingly soluble in the latter solvent. The pale yellow needles melted at 278·5° with decomposition (Found: in material dried at 100°, S = 8·4. $C_{19}H_{17}O_6NS$ requires S = 8·3 per cent.). The aqueous or alcoholic solutions of this methosulphate exhibit a striking violet fluorescence. On the addition of sodium hydroxide to an aqueous solution, a curdy green precipitate was thrown down. This turned brown and then black in contact with air, but retained its original colour in an atmosphere of hydrogen. All attempts to crystallise the compound were unsuccessful, and the carefully washed and dried substance was analysed (Found: C = 72·4; H = 5·0; N = 3·8 per cent.). These figures do not accord with any simple formula, but the percentage of carbon clearly shows that the substance is not derived from the methohydroxide by loss of water.

6 : 7-*Methylenedioxy*-2 : 3-*indeno*(2 : 1)-*quinoline* (XI).

6-Aminopiperonal (2·9 grams) and β-hydrindone (2·5 grams) were dissolved in ethyl alcohol (35 c.c.) and aqueous potassium hydroxide (20 c.c. of 33 per cent.) added. In a few minutes the quinoline derivative separated as a voluminous mass of pale yellow needles and was collected, washed, and dried at 100°. The yield was 84 per cent. of that theoretically possible. The substance is moderately readily soluble in organic solvents with the exception of light petroleum and may be crystallised from benzene. It melts at 215·5° and resembles in its properties the isomeride described above except for the indications of the existence of an azonoid form which are discussed on p. 830 (Found: C = 78·0; H = 4·4; N = 5·6. $C_{17}H_{11}O_2N$ requires C = 78·2; H = 4·2; N = 5·4 per cent.).

The sparingly soluble *hydrochloride* crystallises in pale yellow needles and its aqueous or alcoholic solutions exhibit intense purple fluorescence.

Methosulphate.—This derivative crystallises in almost theoretical yield from a boiling benzene solution of the base and excess of neutral methyl sulphate. It separates from a hot solution in ethyl alcohol in slender, yellow needles which begin to decompose at 257° (Found: S = 8·4. $C_{19}H_{17}O_6NS$ requires S = 8·3 per cent.).

Methochloride.—The methosulphate is dissolved in hot, moderately concentrated hydrochloric acid and on cooling the chloride

crystallises in pale yellow, glistening needles which commence to decompose at 195° and are quite black at 235°.

The aqueous solutions of the methosulphate and methochloride exhibit a reddish-violet fluorescence of phenomenal intensity and persistence on dilution.

Anhydro-6 : 7-*methylenedioxy*-2 : 3-*indeno*(2 : 1)-*quinoline Methohydroxide* (XII).

This interesting substance was obtained as a copious purple precipitate by the addition of potassium hydroxide to an aqueous solution of the methosulphate described in the immediately preceding section. The substance was collected, washed with water, and dried at 70°. It is moderately readily soluble in most organic solvents to intense bright purple solutions and crystallises from dry ether or from ethyl acetate in deep indigo, hexagonal prisms, melting at 170° (Found: C = 78·7; H = 4·5; N = 5·3. $C_{18}H_{13}O_2N$ requires C = 78·6; H = 4·7; N = 5·1 per cent.).

The substance is very stable, but is gradually hydrated in presence of an excess of boiling water, yielding a yellow, fluorescent, alkaline solution of the methylenedioxyindenoquinoline methohydroxide. It is readily changed by acids to the corresponding metho-salts. Thus the hydrochloride was prepared and obtained in yellow needles, decomposing at 195—235°, which were proved by a careful comparison to be identical with the methochloride of methylenedioxy-2 : 3-indeno-(2 : 1)-quinoline.

Anhydro-6 : 7-*methylenedioxy*-2 : 3(3-*methylindeno*)(2 : 1)-*quinoline Methohydroxide* (XIII).

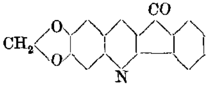
The anhydro-base (1·0 gram) described in the last section was boiled under reflux with methyl iodide (76 grams) during seven and a half hours. The reaction proceeded very slowly, but the purple colour of the solution had disappeared after one hour. The yellow precipitate was removed by filtration and was stable when dry, whilst in the moist condition, in contact with air, it had a great tendency to form a bright green substance. This methiodide was suspended in hot water and converted to chloride by the action of an excess of freshly precipitated silver chloride. The filtered solution was concentrated to a small bulk and the chloride thrown down as an ochre precipitate by the addition of common salt. The substance was collected and crystallised from dilute hydrochloric acid, being obtained in light ochre-yellow, microscopic, rhombic prisms (*A*).

The mother-liquors on concentration gave a further crop of needle crystals. These were recrystallised from dilute hydro-

chloric acid, and from the appearance of the yellow needles under the microscope and the fact that they decomposed at 195—235° evidently consisted of methylenedioxyindenoquinoline methochloride derived by the action of hydrochloric acid on unchanged anhydro-base. The survival of some of the latter in the reaction is probably due to the coating of a few of the crystals by the methiodide formed. Crop *A* was dissolved in water and, on the addition of sodium hydroxide, gave a purple precipitate which was collected, washed with very little water, and dried in a vacuum. The substance crystallised from anhydrous ether in intense purplish-black aggregates of rectangular prisms, which exhibit bronze lustre and soften and decompose at 195°. It is moderately readily soluble in most organic solvents, but sparingly soluble in light petroleum (Found: C = 78·8; H = 5·0. $C_{19}H_{15}O_2N$ requires C = 78·9; H = 5·2 per cent.).

An ethyl acetate solution of this base is deep red purple, and on shaking with water is decolorised, the aqueous solution exhibiting bright reddish-violet fluorescence. The substance is more easily hydrated to the related methylquinolinium hydroxide than is the lower homologue, and this is in harmony with similar observations in the *iso*papaverine series. It dissolves in acids to intensely fluorescent solutions, and the hydrochloride crystallises in yellow, rhombic prisms identical in appearance under the microscope with those constituting the crop *A* mentioned above.

6 : 7-*Methylenedioxy*-2 : 3(3-*ketoindeno*)(1 : 2)-*quinoline*,



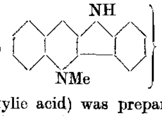
A solution of 6-aminopiperonal (2·4 grams) and 1 : 3-diketohydrindene (2·9 grams) in 80 per cent. acetic acid (35 c.c.) was boiled during ten minutes, when the whole became pasty owing to the separation of the condensation product. The substance was collected, washed, dried (2·8 grams), and crystallised from hot benzene, from which it separated in yellow needles melting at 242° (Found: C = 74·3; H = 3·0; N = 5·1. $C_{17}H_9O_3N$ requires C = 74·2; H = 3·3; N = 5·1 per cent.).

If the condensation is carried out in glacial acetic acid, an intermediate product is obtained in deep blue crystals with green reflex. This substance has affinity for animal fibres and is dichroic in alcoholic solution, thin layers being blue and thick layers red. It is converted into the quinoline derivative by boiling dilute acetic

acid. Methylenedioxyketoindenoquinoline is readily soluble in chloroform, moderately soluble in benzene; it dissolves sparingly in alcohol or ether, and is almost insoluble in light petroleum. It is a feeble base, soluble in dilute mineral acids to non-fluorescent, yellow solutions.

Methosulphate.—This derivative was found to be difficult to obtain owing to the feebly basic character of the quinoline ketone. It was prepared by prolonged boiling of a benzene solution of the base and excess of methyl sulphate. The substance crystallised from ethyl alcohol, in which it is sparingly soluble, in well-shaped, intensely yellow, rhombic prisms, which begin to decompose at 266° and melt at 275° with decomposition (Found: S = 8·0. $C_{20}H_{19}O_6NS$ requires S = 8·0 per cent.). The salt is readily soluble in water, but the solution does not exhibit fluorescence. On the addition of sodium hydroxide, a crimson precipitate was thrown down. This was collected, washed, dried, and crystallised from a mixture of benzene and light petroleum. The substance was obtained in minute, red needles, readily soluble in benzene or chloroform, less soluble in alcohol or ether, and very sparingly soluble in light petroleum. On heating, it darkens at 105° and decomposition progresses above this temperature, although the substance only melts at 198—199°. The analytical results could not be reconciled with a simple formula and agreed approximately with the percentages required by the methohydroxide with $\frac{1}{2}H_2O$.

Reduction of the ketoquinoline by means of zinc dust in glacial acetic acid solution gave a base which forms a sparingly soluble hydrochloride, the aqueous solution of which exhibits intense bluish-violet fluorescence. The base is, however, not identical with methylenedioxyindenoquinoline and may be the secondary alcohol corresponding with the ketone.

Quindoline Methosulphate,  SO_4Me.

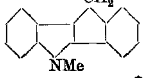
Flavindine (quindolinecarboxylic acid) was prepared in almost theoretical yield by boiling isatinic acid (1 mol.) with an alkaline solution of the technical indoxyl fusion (containing 1 mol. of indoxyl) in an atmosphere of coal gas. It was quantitatively converted into quindoline by successively reducing in aqueous solution with sodium amalgam and shaking with air, this process being more convenient than that of Fichter and Rohner (*Ber.*, 1910, **43**, 3489), who reduced flavindine by means of zinc dust and sodium hydroxide. Quindoline (10 grams) was dissolved in the

least possible amount of boiling benzene and methyl sulphate (15 grams) added in one portion. The deep orange solution which resulted soon deposited a light orange precipitate, and after boiling for half an hour the liquid was cooled and the solid collected, washed with benzene, and crystallised from ethyl alcohol. It was obtained in long, orange-yellow needles which lost solvent of crystallisation at 100°, leaving an orange-yellow powder (Found: C = 59·9; H = 4·7; N = 8·5. $C_{17}H_{16}O_4N_2S$ requires C = 59·3; H = 4·6; N = 8·1 per cent.).

The substance is readily soluble in water to an intense yellow solution and moderately soluble in ethyl alcohol. It melts at 242—245° without perceptible decomposition. On treatment with alkali in aqueous solution, a curious, chalky, mauve precipitate was thrown down. The substance was washed and dried, and gave results on analysis which were in accord with those required by the methohydroxide with from 2·4 to 1·6 mol. H_2O in different specimens. The substance crystallises very well from aqueous acetone containing a little sodium hydroxide in slender, mauve-red threads, which decompose slowly at 100°. This product was thoroughly washed and dried in a vacuum over phosphoric oxide (Found: C = 73·2, 73·5; H = 6·0, 6·0; N = 9·6. $C_{35}H_{36}O_4N_4$ requires C = 73·8; H = 6·2; N = 9·7 per cent.).

The formula of methylquindolinium hydroxide is $C_{16}H_{14}ON_2$, and this substance may therefore be $2C_{16}H_{14}ON_2,C_3H_6O,H_2O$, or possibly *di(methylquindolyl)acetone* with $3H_2O$. When freshly prepared, it is changed by dilute hydrochloric acid to methylquindolinium chloride, which was identified with the salt described below, but it apparently suffers decomposition on keeping and, after three months, a specimen was found to give dark oily products on similar treatment.

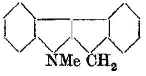
Quindoline Methochloride.—This salt crystallised in slender, fibrous needles on cooling a hot solution of the methosulphate in dilute hydrochloric acid. The bright canary-yellow substance becomes orange at about 180—200° and melts with decomposition at 273° (Found: in material dried at 120°, Cl = 13·2. $C_{16}H_{13}N_2Cl$ requires Cl = 13·1 per cent.). This derivative is more sparingly soluble in cold water than is the methosulphate, but dissolves readily in hot water. On the addition of a drop of hydrobromic acid, the corresponding bromide is precipitated in radiating clusters of yellow needles.

1-*Methyl*-2 : 3-*indeno*(1 : 2)-*indole*, .

as-Phenylmethylhydrazine (4·6 grams) was added to a solution of α-hydrindone (5 grams) in glacial acetic acid (50 c.c.), when after a short time the hydrazone separated as a bulky, crystalline precipitate. After allowing to remain fifteen minutes, concentrated hydrochloric acid (50 c.c.) was added, producing a blood-red coloration, and the formation of the indole derivative completed by heating on the steam-bath during fifteen minutes. The orange paste was filtered and the solid washed with water and alcohol and dried at 70° (6·5 grams). The substance is moderately soluble in alcohol, benzene, or acetone, sparingly soluble in light petroleum, and is best crystallised from alcohol, being obtained in colourless platelets melting at 153·5° (Found: N = 6·6. $C_{16}H_{13}N$ requires N = 6·4 per cent.).

2 : 3-*Indeno*(2 : 1)-*indole*, .

The phenylhydrazone which separated from a mixture of β-hydrindone (1·3 grams), phenylhydrazine (1·5 grams), and acetic acid (20 c.c.) was collected and heated during fifteen minutes with concentrated hydrochloric acid (35 c.c.) on the steam-bath. Water was added, the precipitate filtered off, washed, and crystallised from ethyl alcohol. The yield of crystallised substance amounted to 1·1 grams. For analysis, the compound was crystallised from benzene and obtained in hexagonal double pyramids, which begin to decompose at about 200° and melt at 212—215° (Found: C = 87·5; H = 5·5; N = 6·9. $C_{15}H_{11}N$ requires C = 87·8; H = 5·4; N = 6·8 per cent.). This substance is readily soluble in organic solvents and exhibits bluish-green fluorescence in alcoholic solution.

1-*Methyl*-2 : 3-*indeno*(2 : 1)-*indole*,  .

This indole derivative was prepared from β-hydrindone exactly as described above for the corresponding compound derived from α-hydrindone. The yield was 59 per cent. of that theoretically possible. The substance crystallised from ethyl alcohol, in which it is moderately readily soluble, in rhombic prisms melting at 172° (Found: C = 87·6; H = 5·9; N = 6·6. $C_{16}H_{13}N$ requires C = 87·7; H = 5·9; N = 6·4 per cent.).

Like the two other indole derivatives described above, this substance does not exhibit characteristic indole reactions. It is readily soluble in chloroform, benzene, or acetone, sparingly soluble

in ether, and very sparingly soluble in light petroleum. Further experiments relating to these indenoindoles are in progress.

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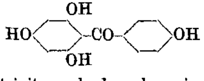
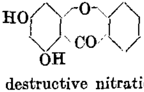
United College of St. Salvator and St. Leonard,
The University, St. Andrews. [*Received, April 3rd*, 1922.]

XCIV.—*The Hydroxybenzoylphloroglucinols.*

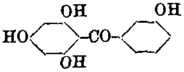
By Hidejiro Nishikawa and Robert Robinson.

Some ten years ago, one of us, in collaboration with Mr. H. G. Smith, commenced an investigation of eudesmin and aromadendrin, two highly characteristic and readily purified substances discovered by Maiden and Smith (*J. Roy. Soc. New South Wales*, 1895, **29**, 30) in the kino of *Eucalyptus hemiphloia*, and later found to occur separately or together in the kinos of many other species of *Eucalyptus*; for example, *E. calophylla*, R.Br., produces a kino which contains aromadendrin but no eudesmin (Smith, *ibid.*, 1896, **30**, 135). The research on the constitution of aromadendrin is not yet completed, but in order to explain the object of the work described in the present communication a few of the results may be outlined, leaving the details for the subsequent publication of Smith and Robinson, which, it is hoped, may not be long delayed. Aromadendrin contains no methoxyl groups and is optically inactive. It yields phloroglucinol on fusion with alkali, and picric acid on boiling with nitric acid. Its formula is $C_{13}H_{10}O_5$ or $C_{18}H_{14}O_7$, and whereas the latter is now regarded as correct, the former was at one stage considered the more probable of the two. Believing this, it was obvious that aromadendrin should be 2 : 4 : 6 : 4′-tetrahydroxybenzophenone (I), since the *m*-hydroxybenzoylphloroglucinol would

(I.) 

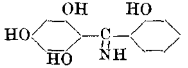
(II.) 

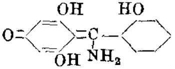
yield trinitro-*m*-hydroxybenzoic acid on destructive nitration and the ortho-derivative should readily lose water under appropriate conditions with the formation of 1 : 3-dihydroxyxanthone (II). Such a transformation of aromadendrin could not be realised. In any case it appeared desirable to attempt the preparation of the three hydroxybenzoylphloroglucinols, because even if none of them

(III.) 

is identical with aromadendrin, the para-isomeride especially is quite likely to be obtained from natural sources, bearing, as it does, the relation to maclurin that apigenin bears to luteolin and kaempferol to quercetin.

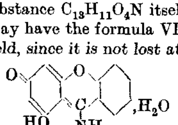
2 : 4 : 6 : 3′-Tetrahydroxybenzophenone (III) and 2 : 4 : 6 : 4′-tetrahydroxybenzophenone (I) have been synthesised by the condensation of phloroglucinol with *m*-hydroxybenzonitrile and *p*-hydroxybenzonitrile, respectively, in accordance with the general method devised by Hoesch (*Ber.*, 1915, **48**, 1122). They both resemble aromadendrin in certain respects. The preparation of 2 : 4 : 6 : 2′-tetrahydroxybenzophenone from salicylonitrile and phloroglucinol by an application of the Hoesch synthesis has been recorded by Karrer (*Helv. Chim. Acta*, 1921, **4**, 992), and whilst we have had no difficulty in repeating the experiment, we are unable to confirm Karrer's view of the composition of the product isolated, which we find to be $C_{13}H_{11}O_4N$, and not $C_{13}H_{10}O_5$. Apparently the substance is the ketimine (IV) or the tautomeric aminoquinone (V),

(IV.) 

(V.) 

which is protected from hydrolysis in acid solution by the three hydroxyls in the ortho-positions.

We invariably obtained this substance in yellow needles, whilst Karrer states that his tetrahydroxybenzophenone crystallised in leaflets. In other respects, the description given of the supposed ketone tallies with the properties of this nitrogenous compound. The substance $C_{13}H_{11}O_4N$ is hydrolysed by boiling dilute aqueous sodium hydroxide and ammonia is evolved. On acidifying the solution, 1 : 3-dihydroxyxanthone (II) is precipitated. This decomposition raises the question of the existence or non-existence of the ether bridge in the substance $C_{13}H_{11}O_4N$ itself. It is just possible that this compound may have the formula VI, but in that case the $1H_2O$ is very firmly held, since it is not lost at 140°.

(VI.) 

Experimental.

2 : 4 : 6 : 2′-*Tetrahydroxydiphenyl Ketimine* (Formula IV, V, or VI).

The condensation of phloroglucinol (3 grams) and salicylonitrile by the Hoesch method was carried out as described by Karrer (*loc. cit.*)

and 1·9 grams of the ketimine hydrochloride were obtained. This salt readily dissolved in hot water, but very soon a bright yellow substance separated in prismatic needles, the yield from the salt being quantitative. The substance is nearly insoluble in boiling water and in most organic solvents. It is, however, readily soluble in pyridine and dissolves sparingly in boiling alcohol, crystallising on cooling in golden-yellow needles (0·05 gram from 500 c.c.) which suffer no loss in weight at 140° (Found: C = 64·0; H = 4·7; N = 5·5. $C_{13}H_{11}O_4N$ requires C = 63·7; H = 4·5; N = 5·7 *per cent.*).

On heating, the compound becomes orange at about 220° and darkens above this temperature; above 300°, it blackens, but does not melt. It is insoluble in cold or hot dilute hydrochloric acid, but readily passes into solutiou on the addition of a few drops of alcohol. The *hydrochloride* crystallises in colourless needles from a moderately concentrated solution in hot aqueous alcoholic hydrochloric acid. This derivative is decomposed with production of the ketimine either by boiling with water or by the addition of sodium acetate to a hot solution. The ketimine is extraordinarily resistant to hydrolysis in acid solution, and we were unable to obtain the corresponding ketone. The substance dissolves in concentrated nitric acid to a red solution and in sulphuric acid to an almost colourless solution. The addition of zinc dust to a suspension in hot dilute sulphuric acid produces a pink coloration. Its alcoholic solution is coloured brown by ferric chloride.

1 : 3-*Dihydroxyxanthone* (Formula II).

The tetrahydroxydiphenyl ketimine is readily soluble in dilute aqueous sodium hydroxide, producing a sodium derivative, which separates in a gelatinous form from more concentrated solutions. On boiling, the yellow solution becomes orange and ammonia is evolved. The hydrolysis was carried out by means of an excess of very dilute aqueous sodium hydroxide kept at the boiling point until ammonia was no longer produced. The solution was cooled and acidified with hydrochloric acid; the resulting colourless, gelatinous precipitate became more crystalline on boiling and was then collected and washed. The substance is sparingly soluble in ether, but readily so in alcohol, and was crystallised from aqueous alcohol. It separated in colourless, glistening needles which lost 7·5 per cent. in weight when heated at 110° during three hours (Found: in anhydrous substance, C = 68·3; H = 3·6. $C_{13}H_8O_4,H_2O$ requires H_2O = 7·3 per cent. and $C_{13}H_8O_4$ requires C = 68·4; H = 3·5 per cent.).

1 : 3-Dihydroxyxanthone melts at 259°, after softening at 256°,

and sublimes. It dissolves in concentrated sulphuric acid to a yellow solution exhibiting a weak bluish-green fluorescence, which becomes much more intense after a short time. In concentrated nitric acid it gives at first a dirty green colour and on standing the solution becomes purple. Its alkaline solution is bright yellow. On treatment with zinc dust and hot dilute sulphuric acid it gives a clear rose solution which is rapidly decolorised. The addition of ferric chloride to an alcoholic solution produces a greenish-brown coloration. Kostanecki and Nessler (*Ber.*, 1891, **24**, 3980) have described the preparation of 1 : 3-dihydroxyxanthone along with a hydroxydixanthone by distilling a mixture of phloroglucinol, salicylic acid, and acetic anhydride. They ascribe the melting point 247° to the substance, and do not state that it crystallises with $1H_2O$. Our compound, m. p. 259°, exhibits the characteristic reactions described by Kostanecki and Nessler for the product, m. p. 247°, and in order to remove all doubt as to the identity of these substances we prepared the diacetyl derivatives from specimens obtained by the two methods. The colourless needles melted at 145°, alone or mixed (Kostanecki and Nessler, *loc. cit.*, give 144°).

2 : 4 : 6 : 3′-*Tetrahydroxybenzophenone* (Formula III).

m-Hydroxybenzonitrile (2 grams) and anhydrous phloroglucinol (2 grams) were dissolved in dry ether (20 c.c.) and after the addition of freshly fused and powdered zinc chloride (1 gram) hydrogen chloride was passed into the liquid during two hours. A dark syrup separated and after allowing to remain over-night, sulphuric acid (20 c.c. of 25 per cent.) was gradually added to the cooled mixture. Granular crystals of the ketimine sulphate together with some unchanged material separated and the latter was removed by collecting the precipitate and washing with ether. The salt (2·2 grams) was hydrolysed by boiling for an hour with water (15 c.c.). On cooling and scratching the containing vessel, tetrahydroxybenzophenone (1·5 grams) was obtained in yellow crystals. The substance is best recrystallised from water and separates in pale yellow, thin, narrow leaflets, radially aggregated. The air-dried substance suffers no loss in weight when heated at 130° (Found: C = 63·4; H = 4·2. $C_{13}H_{10}O_5$ requires C = 63·4; H = 4·1 per cent.).

2 : 4 : 6 : 3′-*Tetrahydroxybenzophenone*, when rapidly heated, decomposes at 246° after previous darkening. It is sparingly soluble in ether and readily soluble in alcohol and hot water. Its alcoholic solution is coloured purple by ferric chloride and its alkaline solution is orange. In concentrated sulphuric and nitric acids it yields yellow and red solutions respectively. When reduced with

zinc dust and dilute sulphuric acid, the liquid becomes orange and later colourless.

2 : 4 : 6 : 4′-*Tetrahydroxybenzophenone* (Formula I).

p-Hydroxybenzonitrile (6 grams) and anhydrous phloroglucinol (6 grams) were dissolved in dry ether (36 c.c.), mixed with fused and powdered zinc chloride (3 grams), and a moderate stream of hydrogen chloride was passed through the liquid. Turbidity of the solution occurred after two and a half hours and very soon two layers separated. After four hours the current of gas was stopped and the mixture allowed to remain over-night. Sulphuric acid (60 c.c. of 25 per cent.) was then carefully added and the whole shaken with twice its volume of ether so as to avoid the separation of phloroglucinol. The aqueous solution was separated and gently warmed to remove ether. On cooling, it became filled with a yellow, crystalline mass, the microscopic examination of which revealed admixture with some phloroglucinol. The substance was therefore recrystallised from 25 per cent. sulphuric acid and washed with ether and water (yield = 3·8 grams). This ketimine sulphate occurs in short, yellow needles. The substance was hydrolysed by boiling with water (80 c.c.) under reflux during one and a half hours. The benzophenone derivative (1·8 grams) separated on cooling and was purified by crystallisation from hot water, in which it is rather more readily soluble than the isomeride described in the last section. The substance dried in a vacuum lost 13·0 per cent. at 120°, leaving a yellow powder (Found: in anhydrous substance, C = 63·0; H = 4·4. $C_{13}H_{10}O_5,2H_2O$ requires H_2O = 12·8 per cent., and $C_{13}H_{10}O_5$ requires C = 63·4; H = 4·1 per cent.).

2 : 4 : 6 : 4′-*Tetrahydroxybenzophenone* melts at 210° to a deep red liquid. It crystallises in pale brown prisms, but has also been observed to separate in woolly needles, especially when not quite pure. Its alkaline solution is yellow and it gives a brown colour with ferric chloride in alcoholic solution. Its behaviour with zinc dust and dilute sulphuric acid is similar to that of 2 : 4 : 6 : 3′-tetrahydroxybenzophenone.

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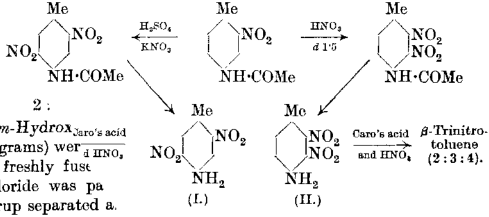
XCV.—*Note on 2 : 3- and 2 : 5-Dinitro*-p-*toluidines.*

By JAMES SCOTT and ROBERT ROBINSON.

IN connexion with a synthetical investigation, which is in progress, we required considerable quantities of 2 : 3-dinitro-*p*-toluidine, the acetyl derivative of which should, it was thought, be the main product of the nitration of the very readily accessible 2-nitroaceto-*p*-toluidide. This was found to be the case if the nitration is conducted by means of nitric acid, but in the presence of sulphuric acid the reaction takes another course, and 2 : 5-dinitroaceto-*p*-toluidide was found to be the chief product. The dinitrotoluidines were orientated by oxidation with Caro's acid to the related trinitrotoluenes as described by Brady in the case of isomerides (T., 1920, **117**, 1139). The following scheme summarises the results :



2 :
m-Hydrox
(2 grams) wer
of freshly fus
chloride was pa
syrup separated a.
acid (20 c.c. of 25 f note at this stage in view of the interest which
mixture. Granular c in the preparation of the complete series of
some unchanged mater are Brady, Day, and Rolt, this vol., p. 526).
collecting the precipitat
grams) was hydrolysed by PERIMENTAL.
On cooling and scratchin (Formula I).—2 : 5-Dinitroaceto-*p*-tolu-
benzophenone (1·5 grams) ble in a gently heated, dilute aqueous
substance is best recrystall le and on standing the dinitrotoluidine
yellow, thin, narrow leaflet in needles. A much more convenient
substance suffers no loss in *following. The acetyl derivative was*
C = 63·4; H = 4·2. $C_{13}H_1$ th a mixture of ten times its weight
cent.).
2 : 4 : 6 : 3′-*Tetrahydroxyben* times its weight of water. The base
decomposes at 246° after p ater and was collected and crystallised
soluble in ether and readily so tained in deep orange-red needles,
alcoholic solution is coloured pu 43·1 ; H = 3·7. $C_7H_7O_4N_3$ requires
solution is orange. In concer This dinitrotoluidine is moderately
yields yellow and red solution ts and more soluble in benzene than

in alcohol. In the former solvent, the solutions are bright canary-yellow, and in the latter are orange-yellow. The substance is a very feeble base, dissolving to some extent in cold concentrated hydrochloric acid to a yellow solution. It dissolves on heating and is precipitated on the addition of water. Such a finely divided precipitate is attacked in the presence of dilute hydrochloric acid by nitrous acid, a clear yellow solution being produced. On the addition of sodium acetate, a purple coloration and then a deep purple precipitate appear. The colour is not entirely discharged by the addition of excess of hydrochloric acid. When the diazotised solution is added to dilute sodium hydroxide, the purple substance is not produced and the resulting yellow solution gives no azo-compound on the addition of *R*-salt. In boiling aqueous alcoholic solution the dinitrotoluidine is readily reduced by zinc dust and hydrochloric acid, and the resultiug colourless solution gives a brilliant carmine coloration on the addition of ferric chloride.

Oxidation by means of Caro's Acid.—2 : 5-*Dinitro-p-toluidine* (1·7 grams) dissolved in 80 per cent. sulphuric acid (10 c.c.) was added to a solution of Caro's acid (10 grams of ammonium persulphate in 7 c.c. of sulphuric acid poured on crushed ice) and the mixture allowed to remain over-night. After the addition of water, the nitrosodinitrotoluene (1·25 grams) was collected and heated with nitric acid (12·5 grams, *d* 1·5) until red fumes ceased to be evolved. On cooling and diluting with water, the trinitrotoluene separated, and was crystallised from alcohol. The pale yellow prisms melted at 104°, alone or mixed with an authentic specimen of 2 : 4 : 5-trinitrotoluene. The alcoholic mother-liquors were boiled after the addition of β-naphthylamine, when, very soon, a crystalline precipitate of the characteristic, sparingly soluble 2 : 4-dinitro-5-β-naphthylaminotoluene separated. The substance crystallised from acetic acid in bright red, diamond-shaped prisms, melting at 209°, alone or mixed with a specimen prepared in a similar way from γ-trinitrotoluene.

2 : 5-*Dinitroaceto*-p-*toluidide*. — 2-Nitroaceto-*p*-toluidide (5·1 grams), dissolved in the minimum amount of concentrated sulphuric acid and cooled to 0°, was nitrated by the gradual addition of a solution of potassium nitrate (5·2 grams) in a little sulphuric acid. After the whole had been added, the liquid was allowed to remain during two hours, the containing vessel being surrounded by melting ice. The pale yellow precipitate obtained on the addition of water was collected and crystallised from alcohol (4·9 grams). The substance is readily soluble in the hot solvent, sparingly soluble in the cold, and separates in colourless aggregates of slender needles melting at 132·5° (Found : N = 17·8. $C_9H_9O_5N_3$ requires N = 17·6

per cent.). 2 : 5-Dinitro-*p*-toluidine dissolves in warm acetic anhydride, but is not acetylated. On the addition of a trace of sulphuric acid the acetyl derivative is rapidly produced and was isolated and identified with the product described above.

2 : 3-*Dinitro*-p-*toluidine* (Formula II).—2 : 3-Dinitroaceto-*p*-toluidide was hydrolysed exactly in the manner already detailed in the case of the isomeric 2 : 5-derivative. The substance was crystallised from benzene and then from methyl alcohol, and obtained in orange-yellow needles melting at 124° (Found: C = 42·7; H = 3·9. $C_7H_7O_4N_3$ requires C = 42·6; H = 3·6 per cent.). 2 : 3-*Dinitro*-p-*toluidine* is rather more soluble in organic solvents than is the 2 : 5-dinitro-*p*-toluidine and much less intensely coloured. It is also a slightly stronger base, although all its salts are at once dissociated by water. On reduction with zinc dust and hydrochloric acid in alcoholic solution, a colourless liqnid is obtained, which is coloured dull mauve by the addition of ferric chloride.

Oxidation by means of Caro's Acid.—The oxidation of the dinitrotoluidine was carried out exactly as described above in the case of the oxidation of 2 : 5-dinitro-*p*-toluidine except that the initial reaction with the persulphuric acid solution was allowed to proceed during four days. The product was crystallised from sulphuric acid and from alcohol and obtained in colourless needles melting at 112°, alone or mixed with a specimen of 2 : 3 : 4-trinitrotoluene.

2 : 3-*Dinitroaceto*-p-*toluidide.*—2-Nitroaceto-*p*-toluidide (5 grams) was slowly added, with stirring, to nitric acid (20 c.c., *d* 1·5), the temperature not being allowed to rise above 20°. After two hours, the mixture was added to water and the precipitate collected and dried (5·8 grams). Crystallisation from alcohol gave a product melting at 162—166° which was not quite pure, and at the expense of yield the substance was crystallised from ethyl acetate, being obtained in colourless, silky needles melting at 174·5°. The yield of pure substance amounted to about half the weight of crude product, but considerable amounts of the same compound remained in the mother-liquors, which are being collected and examined (Found: C = 45·3; H = 4·0; N = 17·8. $C_9H_9O_5N_3$ requires C = 45·2; H = 3·8; N = 17·6 per cent.).

CHEMISTRY RESEARCH LABORATORY,
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THE UNIVERSITY, ST. ANDREWS. [*Received, April 6th*, 1922.]

XCVI.—*The Speed of Sulphonation of Phenols. Part I. The Effect of Temperature and the Methyl Group.*

By ARTHUR FRED CAMPBELL.

IN the course of an investigation of the separation of the three cresols from the crude carbolic acid obtained in the coal tar industry, it was learned, from a series of preliminary sulphonation experiments, that under certain definite conditions of reaction *m*-cresol was preferentially and far more readily sulphonated than either *o*- or *p*-cresol.

This important and characteristic property is indicated even when the complex commercial cresylic acid, consisting largely of *o*-, *m*-, and *p*-cresols with small amounts of phenol and the xylenols, is treated with 96 per cent. sulphuric acid at low temperatures. By this means a partial, although very imperfect, separation of *m*-crosol from the crude product may be obtained.

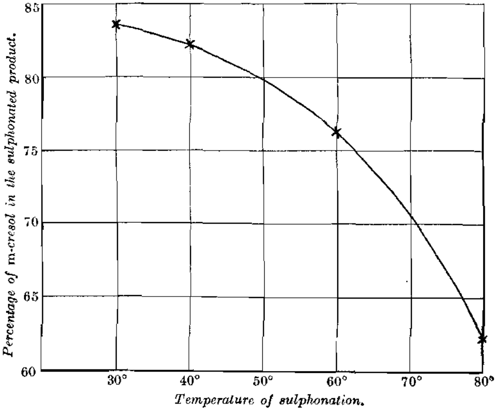
The *sulphonation of m-cresol in preference to the isomeric p*-cresol is still more marked and apparent when a product, obtained by a more complete fractional distillation of the crude carbolic acid, containing no phenol, only traces of *o*-cresol and xylenols, and consisting chiefly of *m*- and *p*-cresols, is treated in a similar manner. Thus by treatment at different temperatures of such a product containing 58—60 per cent. of *m*-cresol with a quantity of concentrated sulphuric acid less than the theoretical amount necessary for complete sulphonation, there is at once a decided preferential sulphonation of *m*-cresol. As the temperature of sulphonation increases, the wide difference, at low temperatures, in the proportion of *m*- to *p*-cresol gradually diminishes until a point *is reached where the ratio is the same as in the original product*, and the two cresols are sulphonated at the same rate. The data obtained by sulphonation for unit time, diagrammatically represented in Fig. 1, where the percentage of *m*-cresol in the sulphonated product is plotted against the temperature of sulphonation, show very clearly that of the three cresols, at least *m*- and *p*-cresols have at low temperatures widely different velocities of sulphonation and that the speed of sulphonation varies considerably with the conditions under which the reaction is carried out.

It is well known that speeds of reaction are extremely sensitive to and readily influenced by variation in temperature. The results tabulated below show that the velocity constant of the sulphonation of phenols is independent *of either the time of reaction*, the concentration, or the amount of sulphuric acid employed. Hence the velocity constant of sulphonation is influenced only by the tempera-

ture of the reaction, and varies considerably according as the sulphonation is carried out at a low or a high temperature.

The following authors should be consulted with reference to formulæ expressing the velocity constant of reactions : Hood (*Phil. Mag.*, 1885, [v], **20**, 323); Warder (*Ber.*, 1881, **14**, 1365); Urech (*ibid.*, 1883, **16**, 765; 1884, **17**, 2174); Spohr (*Z. physikal. Chem.*, 1888, **2**, 195); Hecht and Conrad (*ibid.*, 1889, **3**, 473); van't Hoff, "Études de dynamique chimique," and Arrhenius (*Z. physikal.*

FIG. 1.



Chem., 1889, **4**, 226), who has made a comprehensive study of the reaction velocities in connexion with the inversion of sucrose by acids. Arrhenius gives the following empirical formula, which correctly expresses for irreversible reactions the relation of the influence of temperature on the velocity constant :

$$\frac{d \log_e k}{d T} = \frac{A}{T^2}, \text{ where } A \text{ is a constant.}$$

Perrin (*Ann. Physique*, 1919, [ix], **11**, 6), referring to the influence of temperature on the speed of the reaction, suggests that all chemical reactions are brought about by luminous radiation, and that the speed of reaction is determined by the intensity of the ray and is independent of the temperature except in so far as the intensity depends on it.

The author has been unable to trace any record in the literature of work showing the comparative difference in the velocity constant of the sulphonation of phenols under varying conditions. In this paper the effect of temperature and the methyl group is described.

Since *m*- and *p*-cresols have different velocities of sulphonation at any given low temperature, it is obvious that the relative position of the methyl to the hydroxyl group has a considerable and a definite influence on the resulting speed of sulphonation. Hence it is highly probable that *o*-cresol will have, at any given temperature, a definite comparative speed of sulphonation differing from those of *m*- and *p*-cresols.

The effect on the sulphonation velocity constant produced by the methyl group in different relative positions to the hydroxyl in the benzene nucleus, and also the influence of a second methyl group in the nucleus were determined in experiments with phenol, the three cresols, and certain of the xylenols. The xylenols chosen are of special interest, since they occur in the coal tar fractions allied to the more important cresol fractions.

For this purpose mixtures of pure phenol and *o*-cresol, phenol and *m*-cresol, *o*- and *m*-cresols, *m*- and *p*-cresols, *m*-cresol and *m*-4-xylenol, and *m*-cresol and *p*-xylenol, were treated at different temperatures with 96 per cent. sulphuric acid as described below.

Although the action of concentrated sulphuric acid on the isomeric cresols readily yields either mono- or di-sulphonic acids, only the former are produced under the conditions chosen in this investigation. It is theoretically possible for *o*- and *m*-cresols each to give four monosulphonic acids and for *p*-cresol to give two monosulphonic acids.

Let us consider a system in which the initial concentrations of *o*-, *m*-, and *p*-cresols and sulphuric acid are a, b, c, and m gram-molecules respectively, and after a reaction time t let the concentrations be x, y, z, and n respectively.

During the time t, the above ten monosulphonic acids may be formed, and the products of the reaction may be represented by $q_1, q_2 \ldots q_{10}$ gram-mol.

Hence $\quad a - x = q_1 + q_2 + q_3 + q_4$ gram-mols.,

since q_1 to q_4 are derived from *o*-cresol. Similarly for *m*- and *p*-cresols :

$$b - y = q_5 + q_6 + q_7 + q_8$$

$$c - z = q_9 + q_{10}$$

Also $\quad m - n = q_1 + q_2 + \ldots + q_{10}$

Let $k_1, k_2 \ldots k_{10}$ be the velocity coefficients of the ten possible monosulphonic acid reactions.

The rate of conversion of the cresols into monosulphonic acids will be given by

$$k_1\,n\,x = \frac{dq_1}{dt}\ \text{(ortho)};\ k_5\,n\,x = \frac{dq_5}{dt}\ \text{(meta)};\ \text{and}\ k_9\,n\,x = \frac{dq_9}{dt}\ \text{(para)}.$$

Let $k_A = k_1 + k_2 + k_3 + k_4$; $k_B = k_5 + k_6 + k_7 + k_8$; and $k_C = k_9 + k_{10}$.

Then $k_A\,n\,x = \frac{d\,(a-x)}{dt}$; $k_B\,n\,y = \frac{d\,(b-y)}{dt}$; and $k_C\,n\,z = \frac{d\,(c-z)}{dt}$.

From these equations, by integration, we find:

$$\frac{\log\frac{x}{a}}{\log\frac{y}{b}} = \frac{k_A}{k_B};\quad \frac{\log\frac{y}{b}}{\log\frac{z}{c}} = \frac{k_B}{k_C};\ \text{and}\ \frac{\log\frac{z}{c}}{\log\frac{x}{a}} = \frac{k_C}{k_A}.$$

In the above formulæ k_A, k_B, and k_C are functions of the velocity coefficients of the various possible reactions and are constant for any given temperature. Also a, b, and c are the initial concentrations, and x, y, and z the concentrations after a time t, therefore x/a, y/b, and z/c are the non-sulphonated fractions of *o*-, *m*- and *p*-cresol respectively. Hence the ratio of the logarithms of the non-sulphonated fraction of any two of the cresols at any time t is a constant *dependent only on the temperature of sulphonation.*

The time of reaction and the amount of sulphuric acid employed in the sulphonation do not appear in the formulæ, and therefore the fraction of each non-sulphonated cresol is dependent only on the ratio of their respective velocity coefficients, that is, dependent only on the temperature of sulphonation.

The physical constants given by the various authors for phenol, *o*-, *m*-, and *p*-cresols, and the two xylenols employed in this investigation are summarised below.

	Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.
Boiling point (760 mm.) (*a*) ...	182·2°	191·8°	202·1°	202·5°
Freezing point (*a*)	40·5	30·1	—	36·0
,, ,, (*b*)	41·0	30·45	10·0	34·15
Density at 15·5° (*a*)	—	1·0516	1·0387	1·0388
,, ,, 25°/4° (*b*)	1·0710	1·0415	1·0295	1·0295
Refractive index, $n_D^{40°}$ (*a*)	—	1·53719	1·53322	1·53187
Viscosity, $\eta^{20°}$ (*b*)	0·0883	0·0702	0·1240	0·1413
Solubility in water at 20° (per cent.) (*c*)	8·5	2·8	2·3	2·0

m-4- and *p*-Xylenol melt at 25° and 75° and boil at 208—209° and 209° respectively.

(*a*) Fox and Barker, *J. Soc. Chem. Ind.*, 1917, **36**, 842; 1918, **37**, 269T.

(*b*) Dawson and Mountford, T., 1918, **113**, 937.

(*c*) Sidgwick, Spurrell, and Davies, T., 1915, **107**, 1538.

Experimental.

The phenol, *o*-, *m*-, and *p*-cresols used in this research were coal tar products specially purified by fractional distillation and crystallisation. *m*-4-Xylenol and *p*-xylenol were prepared from the corresponding xylidines. The two xylidines were separated from the commercial mixture of xylidines by the method of Hodgkinson and Limpach (P., 1899, **15**, 202, 213).

In each experiment the stated mixture of phenols was treated with half its weight of 96 per cent. sulphuric acid. In the experiments at 20°, the sulphuric acid was gradually added to the mixed phenols over a period of half an hour. At temperatures at and above 40° the addition was completed in ten minutes. During the addition of the acid the reaction mass was maintained, either by cooling or heating, at approximately 1° below the desired temperature.

The corked flasks were suspended in a water-bath with the body of the flask completely immersed. The temperature of the bath was regulated by a thermostat and maintained at the desired magnitude (± 0·5°) for five hours. The sulphonation mass was poured into water, the non-sulphonated phenols extracted with pure benzene, the combined benzene extracts washed once with water, and the solvent removed by distillation through a Young's four-bulb pear column to 160°. By repeating the distillation three times to 160° the residual phenols contained only an infinitesimal amount of benzene.

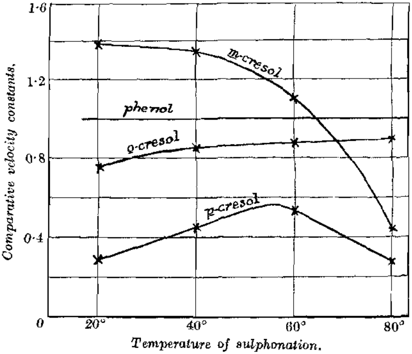
The weighed extract of non-sulphonated phenols was estimated either for phenol or *m*-cresol. In the phenol–*o*-cresol and phenol–*m*-cresol mixtures the phenol was estimated by a determination of the freezing point and the corresponding percentage of phenol read from previously prepared curves. The curves were obtained by plotting the freezing-point determinations of known mixtures of purified phenol and o- and *m*-cresol respectively. To ensure that the freezing point of the product corresponded with a point on the phenol branch of the curve, and well above the eutectic point which occurs in both sets of curves, a mixture of 50 per cent. of pure phenol and 50 per cent. of the product under examination was taken for the determination. Owing to the hygroscopic nature of the substances under consideration it is necessary to take special precautions to eliminate the last traces of water before carrying out the freezing-point determinations.

The curves obtained from the freezing-point determinations of known mixtures of the respective pure products are in very close agreement with those published by Dawson and Mountford (*loc. cit.*).

In the other *m*-cresol mixtures the *m*-cresol was estimated by Raschig's method (*Z. angew. Chem.*, 1900, **14**, 759).

It is usually stated in the literature that the estimation of *m*-cresol in the presence of large amounts of xylenols does not give accurate results, and that the trinitro-compound obtained either melts or forms a soft paste in the steam-oven at 95° to 100°, and refuses to crystallise in the cold. In preliminary experiments carried out with known mixtures of pure *m*-cresol and pure *m*-4-xylenol or pure *p*-xylenol the usual method was found to give concordant results agreeing to within 0·25 per cent. of the *m*-cresol actually taken. In every case the trinitro-compound was definitely crystalline at 100°.

FIG. 2.



The data summarised in Table I represent the mean of several observations of the individual mixtures of phenols. The composition of the mixtures which contain phenol is expressed in terms of weight percentage and molecular percentage. The mixtures of *m*-cresol and the xylenols are similarly expressed. The two series for the isomeric cresols are, of course, identical. The velocity constant is the relative rate of sulphonation of one phenol to the other.

The comparative velocity constants of sulphonation of phenol, *o*-, *m*-, and *p*-cresols at different temperatures are given in Table II.

The comparative velocity constants of the several phenols, with

phenol and *m*-cresol respectively as unity, are plotted against the temperature of sulphonation in Figs. 2 and 3.

FIG. 3.

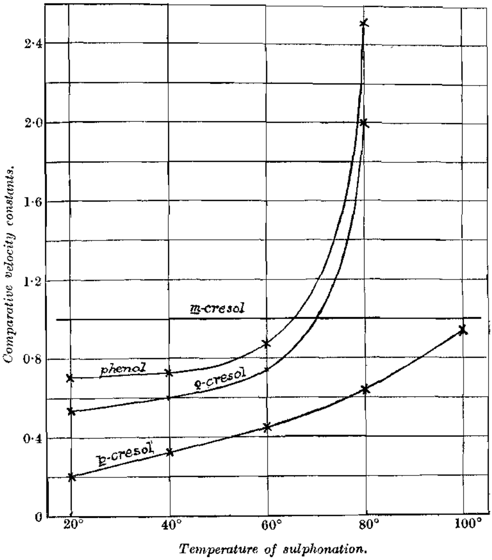


TABLE I.

Phenol–*o*-Cresol.

	Weight per cent.	Molecular percentage.
Phenol	60·0	63·27
o-Cresol	40·0	36·73

Temperature	20°	40°	60°	80°
Non-sulphonated material (per cent.)	52·18	40·16	36·44	37·82
Phenol (per cent.) in non-sulphonated material	56·04	56·80	58·33	59·17
Velocity constant; phenol : *o*-cresol	1·293	1·158	1·118	1·104

Phenol–*m*-Cresol.

	Weight per cent.	Molecular percentage.
Phenol	40·0	43·37
m-Cresol	60·0	56·63

Temperature	20°	40°	60°	80°
Non-sulphonated material (per cent.)	55·74	42·18	39·40	39·30
Phenol (per cent.) in non-sulphonated material	44·60	46·35	42·35	20·15
Velocity constant; phenol : *m*-cresol	0·717	0·723	0·895	2·504

o- and *m*-Cresols.

	Weight and molecular percentage.
o-Cresol	40·0
m-Cresol	60·0

Temperature	20°	40°	60°	80°
Non-sulphonated material (per cent.)	59·60	46·40	38·30	39·30
m-Cresol (per cent.) in non-sulphonated material	52·57	50·86	53·33	75·44
Velocity constant; *m*-cresol : *o*-cresol	1·872	1·665	1·339	0·495

m- and *p*-Cresols.

	Weight and molecular percentage.
m-Cresol	60·0
p-Cresol	40·0

Temperature	20°	40°	60°	80°	100°
Non-sulphonated material (per cent.)	69·40	57·30	51·30	47·50	47·90
m-Cresol (per cent.) in non-sulphonated material	48·8	46·6	47·8	52·6	59·1
Velocity constant; *m*-cresol : *p*-cresol	4·823	3·013	2·230	1·563	1·059

m-Cresol–*m*-4-Xylenol.

	Weight per cent.	Molecular percentage.
m-Cresol	60·0	62·89
m-4-Xylenol	40·0	37·11

Temperature	40°	80°
Non-sulphonated material (per cent.)	49·1	48·6
m-Cresol (per cent.) in non-sulphonated material	42·5	55·7
Velocity constant; *m*-cresol : *m*-xylenol	3·020	1·284

m-Cresol–*p*-Xylenol.

	Weight per cent.	Molecular percentage.
m-Cresol	60·0	62·89
p-Xylenol	40·0	37·11

Temperature	40°	80°
Non-sulphonated material (per cent.)	48·2	34·0
m-Cresol (per cent.) in non-sulphonated material	56·0	66·7
Velocity constant; *m*-cresol : *p*-xylenol	1·260	1·297

TABLE II.

		Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.
At 20°.					
Phenol	to	—	1·293	0·717	3·332
o-Cresol	to	0·773	—	0·534	2·576
m- ,,	to	1·395	1·872	—	4·823
p- ,,	to	0·300	0·388	0·208	—
At 40°.					
Phenol	to	—	1·158	0·732	2·111
o-Cresol	to	0·859	—	0·602	1·813
m- ,,	to	1·362	1·662	—	3·013
p- ,,	to	0·474	0·552	0·331	—
At 60°.					
Phenol	to	—	1·118	0·895	1·862
o-Cresol	to	0·894	—	0·747	1·665
m- ,,	to	1·118	1·339	—	2·230
p- ,,	to	0·537	0·601	0·448	—
At 80°.					
Phenol	to	—	1·104	2·504	3·488
o-Cresol	to	0·905	—	2·015	3·157
m- ,,	to	0·399	0·495	—	1·563
p- ,,	to	0·287	0·317	0·640	—

The closely agreeing results summarised in Table III experimentally show that the velocity constant of sulphonation is independent of either the time or the amount of acid employed in the sulphonation.

In each series of experiments 40 per cent. by weight of *o*- and 60 per cent. of *m*-cresol were treated with the given percentage by weight of sulphuric acid at 40°. In the time experiments the amount of 96 per cent. sulphuric acid was equivalent to half the total weight of cresols. *In the experiments with different amounts* of acid the time of sulphonation was five hours.

TABLE III.

(*a*) Time in hours	1	2	3	4	6
Non-sulphonated material (per cent.)	*56·72*	*52·32*	*50·74*	*50·06*	*48·00*
m-Cresol (per cent.) in non-sulphonated material	53·30	52·20	51·91	52·10	51·55
Velocity constant; *m*-cresol : *o*-cresol	1·663	1·681	1·665	1·630	1·633

(*b*) Acid by weight (per cent.)	35·00	50·00	65·00
Non-sulphonated material (per cent.)	59·18	46·40	31·90
m-Cresol (per cent.) in non-sulphonated material	54·08	50·86	45·91
Velocity constant; *m*-cresol : *o*-cresol	1·627	1·665	1·678

Summary and Discussion of Results.

The influence of the introduction of the methyl group into the phenol molecule on the velocity of sulphonation varies with the

relative position of the methyl to the hydroxyl group and also, but to a different degree, with the temperature of sulphonation.

The methyl group in either the ortho- or para-position to the hydroxyl group has the effect of retarding the speed of sulphonation at all temperatures from 20° to 80°. An *o*-methyl group retards the speed to the least extent and, at 20°, to approximately one-third the degree of a *p*-methyl group.

As the temperature of sulphonation increases, the retarding influence of the *o*-methyl group diminishes somewhat rapidly up to about 60°. Above this temperature the influence is only very slightly progressive. At 80°, and at temperatures above this point, the difference in the comparative speed of sulphonation of phenol and *o*-cresol is almost a constant.

Whilst the methyl group in the ortho- and para-positions to the hydroxyl has the same general effect at all temperatures from 20° to 80°, the methyl group in the meta-position both accelerates and retards the speed of sulphonation according as the reaction is carried out at a lower or higher temperature. A *m*-methyl group has the greatest accelerative effect at low temperatures, and as the temperature increases, the accelerative effect gradually diminishes until at approximately 65° *m*-cresol and phenol are sulphonated at the same rate. Above 65°, a *m*-methyl group has the reverse effect to that at low temperatures and, similar to *o*- and *p*-methyl groups, retards the speed of sulphonation.

The diminished retarding influence of the *o*-methyl group and the reduced accelerative effect of the *m*-methyl group reach a point of equilibrium at about 70°, where the two isomerides are sulphonated at approximately the same rate. Above this temperature *o*-cresol is sulphonated at the quicker rate.

The methyl group in the para-position to the hydroxyl has a greater relative effect, at low temperature, than in either the ortho- or meta-position. As the temperature increases, the retarding influence reaches a minimum at about 60°, and at temperatures above this point again exerts a progressive retardative effect.

The separate effects of the *m*- and *p*-methyl groups reach an equilibrium point at about 100°, where the two isomerides are sulphonated at the same rate.

The following additional data are also established. Phenol is sulphonated at a faster rate than either *o*- or *p*-cresol at all temperatures from 20° to 80°, and at a slower rate than *m*-cresol at temperatures up to about 65°. *p*-Cresol is sulphonated at a much slower rate than either phenol, *o*-cresol, or *m*-cresol at all temperatures up to 80°. At low temperatures *m*-cresol is sulphonated at a greater rate than either phenol, *o*-cresol, or *p*-cresol. Thus,

at 20°, the order of sulphonation is *m*-cresol, phenol, *o*-cresol, and finally *p*-cresol.

The effect of the introduction of the second methyl group into the phenol molecule was observed by the use of *m*-4-xylenol and *p*-xylenol. The two products may be considered as methylated *p*- and *o*-cresols, respectively.

It has been observed above that the methyl group in the ortho- and in the para-position to the hydroxyl in the phenol molecule has a retarding influence on the speed of sulphonation at 40°. Also that the effect of the *p*-methyl group is approximately 3·75 times that of *o*-methyl group. The introduction of the second methyl group in the ortho-position to the hydroxyl in the *p*-cresol molecule should therefore further retard the velocity of sulphonation, and *m*-4-xylenol should be sulphonated at a correspondingly slower rate than *p*-cresol.

The results given in Table II show that phenol is sulphonated at 2·11 times the rate of *p*-cresol, and from the results in Table I it may be calculated that phenol is sulphonated at 2·21 times the rate of *m*-4-xylenol at 40°.

Similarly, the results at 80° confirm the deductions made from the corresponding experiments with the cresols.

p-Xylenol may be considered as *o*-cresol with the second methyl group in the para-position to the methyl and in the meta-position to the hydroxyl group. The results of the experiments with the cresols show that at temperatures up to 65° the methyl group in the meta-position to the hydroxyl has an accelerative effect on the speed of sulphonation; also that a *m*-methyl group has a greater influence than an *o*-methyl group, but in the reverse direction. Therefore the introduction of the second methyl group into *o*-cresol should reverse the order of sulphonation in comparison with that of phenol, and *p*-xylenol should be sulphonated at a faster rate than phenol at 40°.

The results summarised in Table I show that *o*-cresol is sulphonated at 0·859 times the rate of phenol at 40°, and it may be calculated that *p*-xylenol is sulphonated at 1·085 times the rate of phenol at the same temperature. Similar results are obtained at 80°.

It is proposed to determine the influence on the velocity constant of sulphonation of other substituted derivatives of phenol.

In conclusion, the author desires to express his thanks to the directors of Messrs. Hardman and Holden, Ltd., for permission to publish the results.

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XCVII.—*The Determination of Surface Tension from the Maximum Pressure in Bubbles.*

By SAMUEL SUGDEN.

THE determination of surface tension by measurement of the pressure required to liberate bubbles from a vertical capillary tube immersed in a liquid was first suggested by Simon (*Ann. Chim. Phys.*, 1851, [iii], **32**, 5). This method has been largely developed and used by Jaeger as a comparative method (*Sitzungsber. Akad. Wiss. Wien*, 1891, **100**, IIA, 245, 493) and more recently for the absolute determination of the surface tension of a large number of substances (*Z. anorg. Chem.*, 1917, **101**, 1). Cantor (*Wied. Annalen*, 1892, **47**, 399) gave the first accurate theory of the method and used it to obtain absolute surface tensions.* In the literature the name of one or other of the above workers is often employed to denote the method, usually that of Jaeger. Freundlich ("Kapillarchemie," Leipsig, 1909) employs the term "method of maximum bubble pressure," which seems preferable and will be adopted in the present paper.

This method is well adapted for dealing with small amounts of organic substances over a considerable range of temperature. Unfortunately, the results obtained by different observers for many common liquids not only differ among themselves, but are not in agreement with the values found by other methods, for example, the rise in capillary tubes.

These discrepancies may be due to a number of causes, of which the following seem the most important. In the first place, if the liquid has a finite angle of contact with glass, then the method of maximum bubble pressure, which is independent of the contact angle, will give the true surface tension, whilst the method of capillary rise will give lower values which, for small tubes, will be equal to the product of the surface tension and the cosine of the angle of contact. Secondly, this method has often been used as a comparative method, the apparatus being calibrated by means of a standard liquid, for example, benzene or water. Agreement as to the real values of the surface tensions of these liquids has only been reached during the last few years, hence results obtained by the comparative method may be too high or too low,

* See also Linebarger, *Amer. J. Sci.*, 1896, [iv], **2**, 108; Hock, *Sitzungsber. Akad. Wiss. Wien*, 1899, **108**, IIA, 1516; Whatmough, *Z. physikal. Chem.*, 1902, **39**, 129; Feustel, *Drud. Annalen*, 1905, **16**, 6; Forch, *ibid.*, **17**, 744; Ferguson, *Phil. Mag.*, 1914, [vi], **28**, 128; Schroedinger, *Ann. Physik*, 1915, **46**, 413.

according to the value chosen for the standard liquid. The assumption that the surface tension is proportional to the pressure required to liberate bubbles from a given jet is not strictly accurate, but with the small tubes usually employed the error thus introduced is very small. Finally, in the maximum bubble pressure method, it is necessary to correct for the curvature of the larger surface of the liquid. With most liquids it is only when tubes several centimetres in diameter are used that the central portion of the meniscus has a negligible radius of curvature. Except in a few cases, the use of vessels of such a size is impossible and indeed undesirable, for not only does it necessitate the preparation of large quantities of the highly purified liquid, but also the greater area of exposed surface offers more opportunities for contamination with moisture or other impurities. For these reasons, smaller vessels are usually employed, but if no correction is made for the curvature of the surface, the values found for the surface tension will he too small. The magnitude of tbe error thus introduced will depend on the radius of the capillary, and for very small tubes such as those used by Jaeger (*loc. cit.*) is small, but still appreciahle.

It is not easy to deal mathematically with the form of the surface of a liquid in a tube of circular cross-section with another tube placed at its axis. The difficulty can be got over, however, in a similar manner to that employed by the author with the method of capillary rise (T., 1921, **119**, 1483). If two tubes of different radii are immersed to the same depth in a liquid and the pressure required to liberate bubbles from each is measured, then the surface tension can be calculated from the difference of these pressures. It is necessary, however, to have an accurate relationship between the capillary constant of the liquid, the radius of the tube, and the maximum pressure in the bubble, which will hold for tubes up to several millimetres in diameter.

Theoretical.

The theory of the method of "maximum bubble pressure" has been discussed by Cantor, Feustel, Ferguson, and Schroedinger (*loc. cit.*), who corrected certain errors in Cantor's work and gave the formula

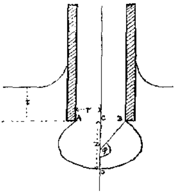
$$a^2 = hr\left(1 - \frac{2}{3}\cdot\frac{r}{h} - \frac{1}{6}\cdot\frac{r^2}{h^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here a^2 is the specific cohesion, r the radius of the capillary tube, and h the maximum pressure in a hubble expressed in cm. of the liquid itself. This formula holds only when r/h is small; to deal with larger tubes it is necessary to have recourse to the tables of

Bashforth and Adams ("An Attempt to Test the Theory of Capillary Action," Camb. Univ. Press, 1883), which give a complete numerical solution of the differential equation involved.

In Fig. 1 AOB represents the outline of a bubble emerging from the end of a vertical tube immersed to a depth t below the surface of a liquid. As the pressure inside the tube is increased, the size and the shape of the bubble change and the angle ϕ between the axis of the tube OC and the normal to the surface of the bubble at B increases. If b is the radius of curvature of the bubble at O, then the pressure in such a bubble is, in $C.G.S.$ units, $p = 2\gamma/b + zg(D - d)$ greater than the pressure at a point in the liquid t cm. below the surface. Here γ is the surface tension in dynes/cm., $z = OC$, g the acceleration due to gravity, D the density of the liquid, and d the density of the gas and vapour inside the bubble. This pressure would be exerted by a column of the liquid of height $h = P/g(D - d)$.

FIG. 1.



Hence (2) $h = \frac{a^2}{b} + z$ and $\frac{hr}{a^2} = \frac{r}{b} + \frac{r}{a} \cdot \frac{z}{b} \cdot \frac{b}{a}$ . . . . (3)

Now the form of the bubble is determined by the value of a quantity β, where

$$\beta = \frac{2b^2}{a^2} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

Putting this in (3), we have

$$(5) \quad \frac{r}{X} = \frac{r}{b} + \frac{r}{a} \cdot \frac{z}{b}\sqrt{\beta/2}, \text{ where } X = \frac{a^2}{h} \quad . \ . \ . \ . \quad (6)$$

For any given value of r/a there will be a number of values of r/X which correspond to a series of values of β, that is, to a series of values of ϕ. These can be calculated from (5) in conjunction with Bashforth and Adams's tables referred to above, as follows.

First, each value of r/b is calculated by the relation

$$\frac{r}{b} = \frac{r}{a} \cdot \frac{a}{b} = \frac{r}{a}\sqrt{2/\beta} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

The angle ϕ corresponding with this value of r/b (the x/b of Bashforth and Adams's tables) and the quantity z/b for this angle are then obtained under the appropriate β from Bashforth and Adams's

tables and inserted in (5) to calculate r/X. The following example will make this clear.

$r/a = 1{\cdot}0$.

β.	r/b.	z/b.	r/X.	ϕ.
6·0	0·5772	0·6756	1·7479	147·1°
6·5	0·5546	0·6640	1·7519	152·6
7·0	0·5346	0·6514	1·7536	157·5
7·5	0·5165	0·6384	1·7528	162·1
8·0	0·5000	0·6254	1·7508	166·5

It will be seen that as ϕ increases, r/X, which is proportional to the pressure in the bubble, passes through a maximum value which can readily be determined. For this value of r/a, which corresponds with a tube 7 mm. in diameter immersed in water, the maximum is reached when ϕ is about 160°. It is only for infinitely small tubes that the maximum pressure corresponds with $\phi = 90°$.*

A series of minimum values of X/r can be calculated in this way for a range of values of r/a and from them, by careful interpolation, Table III has been constructed. For the smallest values of r/a, up to 0·20, the formula of Schroedinger (1) was used. For this value of r/a both methods gave the same result for X/r, but, as would be expected, as r/a increases, this formula no longer holds.

TABLE III.

Minimum value of X/r for values of r/a from 0 to 1·50.

r/a	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·0	1·0000	0·9999	0·9997	0·9994	0·9990	0·9984	0·9977	0·9968	0·9958	0·9946
0·1	0·9934	9920	9905	9888	9870	9851	9831	9809	9786	9762
0·2	9737	9710	9682	9653	9623	9592	9560	9527	9492	9456
0·3	9419	9382	9344	9305	9265	9224	9182	9138	9093	9047
0·4	9000	8952	8903	8853	8802	8750	8698	8645	8592	8538
0·5	8484	8429	8374	8319	8263	8207	8151	8094	8037	7979
0·6	7920	7860	7800	7739	7678	7616	7554	7493	7432	7372
0·7	7312	7252	7192	7132	7072	7012	6953	6894	6835	6776
0·8	6718	6660	6603	6547	6492	6438	6385	6333	6281	6230
0·9	6179	6129	6079	6030	5981	5933	5885	5838	5792	5747
1·0	5703	5659	5616	5573	5531	5489	5448	5408	5368	5329
1·1	5290	5251	5213	5176	5139	5103	5067	5032	4997	4962
1·2	4928	4895	4862	4829	4797	4765	4733	4702	4671	4641
1·3	4611	4582	4553	4524	4496	4468	4440	4413	4386	4359
1·4	4333	4307	4281	4256	4231	4206	4181	4157	4133	4109
1·5	4085									

By the aid of Table III the surface tension can be calculated accurately from the pressures required to liberate bubbles from *two tubes of different radii which are immersed to the same depth* below the surface of the liquid. Let r_1, r_2 be the radii of the tubes, h_1, h_2 the pressures, measured in cm. of the liquid concerned,

* Compare Ferguson, Schroedinger, *loc. cit.*

which are required to liberate bubbles, and t the depth to which each tube is immersed. Then from (6)

$$h_1 = \frac{a^2}{X_1} + t, \quad h_2 = \frac{a^2}{X_2} + t.$$

Therefore $H = h_1 - h_2 = a^2(1/X_1 - 1/X_2)$

or $$a^2 = \frac{H}{1/X_1 - 1/X_2} \quad . \quad . \quad . \quad . \quad (8)$$

The use of this equation and the table are best explained by means of an example. With the apparatus described in the experimental part of this paper the following values were found for benzene at 20° : $r_1 = 0{\cdot}007525$ cm., $r_2 = 0{\cdot}0600$ cm., $H = 6{\cdot}81$ cm. of water at 15° = 7·755 cm. of benzene at 20°.

As a first approximation, take $X_1 = r_1$, $X_2 = r_2$.

Then $$a^2 = \frac{7{\cdot}755}{116{\cdot}2} = 6{\cdot}675 \text{ sq. mm.}$$

Using this value of a^2 to calculate r_1/a and r_2/a, it is found that

$$r_1/a = 0{\cdot}029 \qquad r_2/a = 0{\cdot}232.$$

From Table III the corresponding values of X/r are

$$X_1/r = 0{\cdot}9994 \qquad X_2/r = 0{\cdot}9649,$$

whence $$X_1 = 0{\cdot}007522 \qquad X_2 = 0{\cdot}0579.$$

Putting these values in (7), $a^2 = 6{\cdot}703$ sq. mm.

A further application of this method of successive approximations gives the same result for a^2.

At 20°, for benzene, $D - d = 0{\cdot}8771$, $g = 981$ cm./sec.^{2}, from which $\gamma = 28{\cdot}84$ dynes/cm.

This method of calculation need not be used for every measurement, but constants for a particular apparatus may be calculated as follows.

Let $$P = Hg(D - d) \quad . \quad . \quad . \quad . \quad (9)$$

Then from (8)

$$\gamma = \frac{P}{2(1/X_1 - 1/X_2)} \quad . \quad . \quad . \quad . \quad (10)$$

Now the denominator of (10) is a function of r_1/a and r_2/a, and if r_1 and r_2 are fixed for a given apparatus, then this quantity is a function of $1/a$, which is a function of $g(D - d)/P$.

If a number of arbitrary values of H and $D - d$ are chosen and γ is calculated for each by the method given above, the value of the denominator in (10) can be plotted against $g(D - d)/P$.

In the table below this has been done for apparatus (2) above.

H cm.	$D - d$ grams/c.c.	P dynes.	γ dynes/cm.	P/γ.	$\frac{gD}{P}$.
5	1·000	4905	26·56	184·67	0·2000
7	,,	6867	36·95	185·88	0·1429
10	,,	9810	52·54	186·74	0·1000
15	,,	14720	78·54	187·42	0·0667
20	,,	19620	104·48	187·80	0·0500
∞	—	—		188·78	0

If a curve be plotted with the figures in the last two columns as co-ordinates, the points will be found to lie almost exactly in a straight line, so that for this apparatus

$$\gamma = \frac{P}{188{\cdot}78 - 20{\cdot}6\, g(D - d)/P} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

This formula is well suited to the calculation of a number of results with the same apparatus. As an example of its use we may take the figure for benzene, for which $P = 5{\cdot}46$ cm. of water at 15° = 5346 dynes per sq. cm.; $D - d = 0{\cdot}8771$; hence $gD/P = 0{\cdot}161$.

Therefore $\gamma = \dfrac{5346}{188{\cdot}78 - 20{\cdot}6 \times {\cdot}161} = 28{\cdot}82$ dynes/cm.

If calculated by the method on p. 862, $\gamma = 28{\cdot}84$.

It is seen at once from this formula that the density need not be known very accurately. An error of 1 per cent. in the density produces an error of 0·1 per cent. in the surface tension.

Experimental.

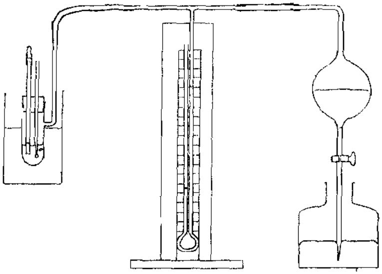
A simple form of apparatus for the measurement of surface tension by the method of "maximum pressure" is shown in Fig. 2. Through a rubber stopper in the vessel A pass two tubes, one of which is drawn out to a fine capillary at its lower end. The other has a diameter of about 3 mm. and is cut off accurately at right angles, with the inner edge sharp and free from splinters. This condition was attained by marking the tube lightly with a file and breaking off a portion in the usual manner. After a few trials, suitably cut tubes were readily obtained.

The side tube of A is connected with a simple pressure gauge, B, and a mercury suction bulb, C. Since small differences of pressure only are concerned, these connexions were made with thick-walled rubber tubing, which was found to be quite satisfactory. Water was used as gauge liquid because of its small coefficient of expansion; the temperature of the gauge was read at intervals during the experiment by means of a thermometer placed beside the

scale and shielded from the heat of the bath in which A was immersed.

In making measurements, the upper end of one of the tubes in A was closed by a stopper and the tap of the mercury suction bulb opened. As the mercury flowed from the bulb, air was sucked in through the open tube in A and finally bubbles formed and broke away from its lower end. The rate of formation of bubbles depends on the size of the capillary jet of the suction bulb; if this be of suitable size, adequate control is obtained by manipulating the tap. In most experiments, the rate of bubble formation on the capillary tube was reduced to one per second

FIG. 2.



before measurements were made. A more rapid rate of bubbling gave the same reading on the gauge as long as the bubbles could be counted easily; more rapid production of bubbles gave appreciably higher readings. With the wide tube the attainment of a maximum pressure which fell off before the bubble was detached could readily be followed on the gauge.

The calibration of the tubes proved to be the most difficult operation. The diameter of the wider tube was measured by means of a reading microscope with a filar micrometer eyepiece. The fine tubes were made by drawing out ordinary quill tubing and were measured as follows. A fine scratch was made with a diamond about 3 mm. from the end and the lower portion grasped in tweezers and bent sharply. The portion broken off in this way was immediately mounted in plasticine on a microscope slide with the newly formed section uppermost. This section and the end of the tube to be used for the measurements were then examined under the microscope to see if the break was clean. Contrary to

expectation, in most cases no splintering occurred and a sharply cut section at right angles to the axis of the tube was obtained. The cut-off portion on the slide was then measured with a suitable objective (usually ¼ inch) and the filar micrometer eyepiece. All tubes which showed more than a slight deviation from a circular cross section were rejected.

In these measurements the standard of length was a Leitz stage micrometer divided into 0·01 mm. This was finally compared with a finely ruled scale on platinum, mounted in Invar, which had been calibrated at the Board of Trade.

Three sets of tubes were used, with the following radii: apparatus 1, $r_1 = 0{\cdot}007796$, $r_2 = 0{\cdot}162$; apparatus 2, $r_1 = 0{\cdot}009934$, $r_2 = 0{\cdot}159$; apparatus 3, $r_1 = 0{\cdot}007525$, $r_2 = 0{\cdot}0600$ cm.

Results.

Measurements were made of the surface tension of water and benzene, as the values for these liquids at 20° are now known accurately. The samples used were purified as described in a previous communication (T., 1921, **119**, 1483). The following values were found:

	For water at 20°. $D-d=0{\cdot}9971$.			For benzene. $D-d=0{\cdot}8871$.		
Apparatus.	H in cm.	a^2 in sq. mm.	γ in dynes per cm.	H in cm.	a^2 in sq. mm.	γ in dynes per cm.
1	18·09	14·90	72·90	8·09	6·720	28·91
2	13·97	14·92	72·96	6·21	6·703	28·84
3	17·25	14·87	72·77	7·755	6·703	28·84
		Mean	72·91		Mean	28·86

These figures are in excellent agreement with those found, by the method of capillary rise, by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) (water, 72·74; benzene, 28·88 and 28·79), Harkins and Brown (*ibid.*, 1919, **41**, 499) (72·80 and 28·88), and Sugden (T., 1921, **119**, 1483) (72·70 and 28·85).

This agreement gives further support to the view of Richards (*loc. cit.*) that for these liquids the angle of contact with glass is zero.

By the method of maximum bubble pressure Jaeger (*loc. cit.*) has found, for water at 20°, $\gamma = 72{\cdot}6$ dynes per cm. The radius of the vessel holding the liquid was about 1·5 cm. Neglecting the influence of the capillary in the centre of the tube, a minimum correction can be calculated. The radius of curvature of the large surface can be calculated by the aid of Table II of the author's paper on the method of capillary rise and with water corresponds with a pressure of 5·9 dynes per sq. cm. For the capillary of radius 0·04385 cm. used by Jaeger this gives a minimum correction

of 0·13 dyne to be added to the observed surface tension. Hence Jaeger's figure agrees satisfactorily with those previously quoted. It should be noted that this correction increases rapidly as the radius of the vessel decreases; if a vessel of half this radius had been used, it would have amounted to 1·70 dynes.

Interpolation between Jaeger's figures for benzene gives $\gamma = 28{\cdot}5$ dynes per cm. at 20°. It should be noted, however, that, contrary to the results of other observers, the surface tension-temperature curve found by Jaeger for this liquid between 5° and 80° deviates appreciably from a straight line. The correction for the large surface in this case is much less than 0·1 dyne and can be neglected.

Summary.

1. The theory of the method of maximum bubble pressure has been extended to apply to tubes for which $r/a = 1{\cdot}5$ (for water, up to tubes 11 mm. in diameter).

2. With a simple form of apparatus measurements of the surface tension of water and benzene have been made with results in satisfactory agreement with those obtained by the method of capillary rise.

BIRKBECK COLLEGE,
CHANCERY LANE, E.C.4. [*Received, March 23rd*, 1922.]

XCVIII.—*The Action of Amines on Semicarbazones. Part I. Preparation of an Optically Active Semicarbazide.*

By FORSYTH JAMES WILSON, ISAAC VANCE HOPPER, and ARCHIBALD BARCLAY CRAWFORD.

IT has been shown by Borsche and his collaborators (*Ber.*, 1901, **34**, 4299; 1904, **37**, 3177; 1905, **38**, 831) that semicarbazones, such as acetonesemicarbazone, for example, react with aromatic amino-compounds on heating, mainly according to the scheme $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + R{\cdot}NH_2 = CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NHR + NH_3$, this product yielding on hydrolysis the semicarbazide $NH_2{\cdot}NH{\cdot}CO{\cdot}NHR$. The action of aniline, the toluidines, the naphthylamines, and similar amino-compounds was studied by Borsche, but the action of aliphatic amines or of aromatic amines containing the amino-group in a side chain does not appear to have been investigated.

It has been found that benzylamine reacts with acetonesemicarbazone in the normal manner, yielding *acetone-δ-benzylsemicarbazone*, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$. Hydrolysis of this sub-

stance with dilute hydrochloric acid gave the *hydrochloride* of δ-benzylsemicarbazide, $NH_2 \cdot NH \cdot CO \cdot NH \cdot CH_2Ph,HCl$, from which the free *base* was liberated by means of sodium ethoxide. In aqueous solution, the hydrochloride reacted readily with benzaldehyde, giving *benzaldehyde-δ-benzylsemicarbazone*.

The action of α-phenylethylamine on acetonesemicarbazone was next studied. The racemic base was first employed and was found to react in the normal manner, the *hydrochloride* of racemic δ-α-phenylethylsemicarbazide, $NH_2 \cdot NH \cdot CO \cdot NH \cdot CHMePh,HCl$, being ultimately obtained. The reaction was then carried out with *d*-α-phenylethylamine; this with acetonesemicarbazone yielded a *semicarbazone*, $CMe_2{:}N \cdot NH \cdot CO \cdot NH \cdot CHMePh$, which, when polarimetrically examined in alcoholic solution, gave $[\alpha]_D^{13} - 67 \cdot 3°$. This semicarbazone on hydrolysis with dilute hydrochloric acid gave the *hydrochloride* of an active δ-α-phenylethylsemicarbazide; this salt in aqueous solution gave $[\alpha]_D^{12} + 66 \cdot 0°$.

It is intended to apply this optically active semicarbazide to the resolution of certain racemic aldehydes and ketones. The only optically active semicarbazide hitherto described appears to be camphoryl-ψ-semicarbazide, which was prepared by Forster and Fierz (T., 1905, **87**, 722). It is also hoped to investigate the action of active menthylamine and of esters of amino-acids on semicarbazones.

EXPERIMENTAL.

Action of Benzylamine on Acetonesemicarbazone.

Acetone-δ-benzylsemicarbazone.—When finely powdered acetonesemicarbazone (1 mol.) and benzylamine (slightly more than 1 mol.), heated separately at 180°, were mixed, vigorons reaction ensued and ammonia was evolved. As soon as solution had been effected, the mixture was cooled somewhat, poured into cold water, the viscid mass treated with dilute acetic acid in slight excess to remove unchanged benzylamine, and the product, which quickly solidified, washed with water and extracted with hot alcohol, which dissolved it with the exception of a slight residue of hydrazodicarbonamide. The alcoholic extract, concentrated if necessary and cooled with ice, deposited a small quantity of colourless needles melting at 168°; these, after recrystallisation from alcohol and washing with carbon tetrachloride, melted at 169° and were identified as *s*-dibenzylcarbamide (m. p. 167°) (Found: N = 11·89 per cent.). The alcoholic extract, on further concentration, yielded long, colourless prisms which, after recrystallisation from alcohol, melted at 113°, were moderately soluble in water, soluble in hot alcohol, and extremely soluble in benzene. This substance

was *acetone-δ-benzylsemicarbazone* (Found : N = 20·35. $C_{11}H_{15}ON_3$ requires N = 20·48 per cent.). It dissolved to a colourless solution in concentrated sulphuric acid.

δ-Benzylsemicarbazide Hydrochloride.—The semicarbazone was heated at 50° with twelve times its weight of *N*-hydrochloric acid until solution was effected. The solution was then extracted with ether, and the aqueous portion evaporated to dryness in a vacuum on the water-bath. The white, flaky residue, consisting of the hydrochloride, recrystallised from alcohol, separated as a thick, felted mass of colourless needles easily soluble in water soluble in alcohol, insoluble in ether. It melted at 224—225° (Found : Cl = 17·46. $C_8H_{11}ON_3,HCl$ requires Cl = 17·62 per cent.).

Crude acetone-δ-benzylsemicarbazone containing *s*-dibenzylcarbamide may be conveniently used in this hydrolysis; *s*-dibenzylcarbamide, being sparingly soluble in water, can be easily separated from δ-benzylsemicarbazide hydrochloride.

δ-Benzylsemicarbazide.—To an absolute-alcoholic solution of the hydrochloride an alcoholic solution of sodium ethoxide was added until the solution was alkaline to phenolphthalein. The sodium chloride was filtered off and the filtrate evaporated to dryness at the ordinary temperature by means of a current of dry air free from carbon dioxide. The yellow residue was treated with hot toluene and the filtered extract cooled in ice, when *δ-benzylsemicarbazide* separated as a white powder consisting of small needle-shaped crystals, which were washed with light petroleum and dried in a vacuum. The substance melted at 111°; it was soluble in water, ether, or chloroform, very soluble in alcohol, soluble in hot benzene and in hot toluene, and insoluble in light petrolenm. The aqueous solution is neutral (Found : N = 25·68, 25·64. $C_8H_{11}ON_3$ requires N = 25·45 per cent.). The *benzylidene* derivative was obtained by shaking an aqueous solution of the hydrochloride with a few drops of benzaldehyde and recrystallising the precipitate from alcohol; it separated in beautiful, large, lustrous prisms melting at 139° (Found : N = 16·77, 16·74 $C_{15}H_{15}ON_3$ requires N = 16·60 per cent.).

Action of α-Phenylethylamine on Acetonesemicarbazone.

The α-phenylethylamine was prepared by the reduction of acetophenoneoxime. It was found that the usual method of preparing this oxime (Janny, *Ber.*, 1882, **15**, 2781) could be very much shortened by adding from time to time potassium hydroxide to neutralise the acidity which appeared during the reaction; the oxime invariably separated as a solid and in practically pure

condition when the reaction mixture was poured into vigorously agitated ice-water.

r-*Acetone-δ-α-phenylethylsemicarbazone.*—This was prepared, in the same way as the acetone-δ-benzylsemicarbazone previously described, by adding α-phenylethylamine (1·5 mols.) heated at 180° to acetonesemicarbazone (1 mol.) at the same temperature. The mixture was cooled and acidified with dilute acetic acid after the addition of an equal volume of alcohol and a little ice. On diluting with water, a white precipitate appeared, which was collected, washed with water, and dissolved in the minimum quantity of hot alcohol, from which the semicarbazone separated in colourless prisms on cooling in ice. *Acetone-δ-α-phenylethylsemicarbazone* was very soluble in alcohol or benzene, and almost insoluble in light petroleum, and was best recrystallised from a mixture of benzene and light petroleum. It melted at 114° (Found : N = 19·04. $C_{12}H_{17}ON_3$ requires N = 19·17 per cent.).

r-*δ-α-Phenylethylsemicarbazide Hydrochloride.*—The semicarbazone was heated with about ten times its weight of *N*-hydrochloric acid in a boiling water-bath, and the solntion, when cold, was extracted with ether, the aqueous portion being evaporated to dryness on the water-bath. The residue was recrystallised from absolute alcohol, from which the *hydrochloride* separated in small prisms melting at 165° with decomposition (Found : Cl = 16·47. $C_9H_{13}ON_3,HCl$ requires Cl = 16·47 per cent.).

These experiments were then repeated, using *d*-α-phenylethylamine. The base employed gave $[\alpha]_D^{15}$ + 40·8°.

Active Acetone-δ-α-phenylethylsemicarbazone.—The reaction was carried out in the same way as in the preparation of the racemic semicarbazone, and a similar plan was adopted in working up the product, which was finally recrystallised from light petroleum; a small, insoluble residue remained. The solution deposited beautiful, rhombic prisms of the semicarbazone, which, after recrystallisation, melted at 84°. Sometimes, after a crop of prisms had continued to grow for some time, the supernatant liquid suddenly became cloudy and a white, apparently amorphous precipitate gradually separated. In such a case, as soon as the cloudiness appeared, the supernatant solution was agitated and decanted, and the prisms were washed with a few c.c. of cold *N*-hydrochloric acid, which readily dissolved the amorphous precipitate. From the solution which had been decanted, the precipitate continued to separate for some time, but afterwards prisms again began to appear. At this stage gentle heat was applied, when the prisms redissolved much more readily than the precipitate, which was then filtered off. In this way a separation

could be effected. The precipitate, after recrystallisation from benzene, melted with decomposition at 185°. The quantity was too small for investigation; the substance was possibly a derivative from carbamide.

The active *acetone-δ-α-phenylethylsemicarbazone* was extremely soluble in alcohol or benzene, and moderately soluble in light petroleum (Found: N = 19·57, 19·60. $C_{12}H_{17}ON_3$ requires N = 19·17 per cent.). It was lævorotatory in alcoholic solution: 0·7820 gram in 10 c.c. of alcohol gave $\alpha_D^{12°}$ − 5·26° (l = 1), whence $[\alpha]_D^{12°}$ − 67·3°. Both the racemic and the active semicarbazones became bright red on addition of concentrated sulphuric acid and ultimately gave an orange-coloured solution.

Active δ-α-Phenylethylsemicarbazide Hydrochloride.—The active semicarbazone was heated on the water-bath with ten times its weight of *N*-hydrochloric acid, and the solution concentrated until crystals appeared. After cooling, these were collected, washed with a very little water, dried, and thoroughly washed with benzene. The *hydrochloride* formed beautiful, pearly plates melting with decomposition at 189°, was very soluble in water, soluble in alcohol, and insoluble in benzene (Found: Cl = 16·40. $C_9H_{13}ON_3$,HCl requires Cl = 16·47 per cent.). It was dextrorotatory in aqueous solution: 0·9766 gram in 10 c.c. of water gave $\alpha_D^{12·2°}$ + 6·56°, whence $[\alpha]_D^{12·2°}$ + 66·0°.

In conclusion, we desire to express our thanks to the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this investigation.

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XCIX.—*Reactions of Thiosemicarbazones. Part I. Action of Halogen Compounds.*

By FORSYTH JAMES WILSON and ROBERT BURNS.

THIOSEMICARBAZONES of numerous aldehydes and ketones have been prepared chiefly by Neuberg and Neimann (*Ber.*, 1902, **35**, 2049) and also by Freund and Schander (*ibid.*, p. 2602). These thiosemicarbazones yield metallic derivatives in which the metal is apparently attached to sulphur, $R_2C{:}N{\cdot}NH{\cdot}C(SM){:}NH$ or $R_2C{:}N{\cdot}N{:}C(SM){\cdot}NH_2$. A methylthiol derivative was obtained in the form of a hydriodide from thiosemicarbazide and methyl iodide

by Freund and Paradies (*Ber.*, 1901, **34**, 3114), and may be represented as $NH_2{\cdot}NH{\cdot}C(SMe){:}NH,HI$, or $NH_2{\cdot}N{:}C(SMe){\cdot}NH_2,HI$. Whilst thiosemicarbazide itself and its alkyl derivatives have been studied by several investigators, chiefly by Busch and his collaborators (*Ber.*, 1901, **34**, 320; 1903, **36**, 1362; 1904, **37**, 2318; 1909, **42**, 4596, 4602), comparatively little work has been carried out with the thiosemicarbazones themselves and their metallic derivatives where the reactive $NH_2{\cdot}N$ group of thiosemicarbazide is absent.

In this paper, the behaviour of metallic derivatives of acetonethiosemicarbazone towards halogen compounds has been investigated. The *sodium* derivative of this thiosemicarbazone has not previously been described; it is easily prepared, and was found to be the most suitable metallic derivative for this work.

The action of ethyl iodide on this sodium derivative was first investigated, but no satisfactory product could be obtained, decomposition accompanied by evolution of mercaptan taking place during the reaction. Benzyl chloride, however, gave a stable product crystallising in long, colourless needles of melting point 51—52°. The structure of this compound was shown to be $CMe_2{:}N{\cdot}N{:}C(S{\cdot}CH_2Ph){\cdot}NH_2$; on heating with sodium hydroxide solution, it yielded benzyl mercaptan, ammonia, and acetone. The alternative formula, $CMe_2{:}N{\cdot}NH{\cdot}C(S{\cdot}CH_2Ph){:}NH$, is inadmissible, since treatment with benzenesulphonyl chloride and sodium ethoxide yielded the *sodium* derivative of a sulphonamide, $CMe_2{:}N{\cdot}N{:}C(S{\cdot}CH_2Ph){\cdot}NNa{\cdot}SO_2Ph$. The hydriodide of the methylthiol derivative obtained by Freund and Paradies (*loc. cit.*) would, on this analogy, possess the formula $NH_2{\cdot}N{:}C(SMe){\cdot}NH_2,HI$. Corresponding with this, the sodium derivative of acetonethiosemicarbazone would be $CMe_2{:}N{\cdot}N{:}C(SNa){\cdot}NH_2$.

Hydrolysis of the foregoing *S*-benzylthiosemicarbazone by warming with dilute hydrochloric acid gave acetone and the *hydrochloride* of *S-benzylthiosemicarbazide*, $NH_2{\cdot}N{:}C(S{\cdot}CH_2Ph){\cdot}NH_2,HCl$. This salt, as was also the *sulphate*, $[NH_2{\cdot}N{:}C(S{\cdot}CH_2Ph){\cdot}NH_2]_2,H_2SO_4$, which was prepared, was relatively stable. Attempts were made to obtain the free base from it, but a pure product could not be isolated. The hydrochloride reacted readily with benzaldehyde in aqueous solution, yielding *benzaldehyde-S-benzylthiosemicarbazone*, $CHPh{:}N{\cdot}N{:}C(S{\cdot}CH_2Ph){\cdot}NH_2$.

The action of esters of certain α-halogen-substituted acids on the sodium derivative of acetonethiosemicarbazone was also investigated. In the hope of obtaining an optically active thiosemicarbazone derivative, the action of *l*-menthyl chloroacetate was tried; it was found, however, that menthol was formed during the

reaction and a substance melting at 175—176° was obtained. Ethyl chloroacetate yielded the same substance, which was shown to be a ψ-thiohydantoin derivative of the structure $CMe_2{:}N{\cdot}N{:}C{<}{\begin{matrix}NH{\cdot}CO\\S{-}CH_2\end{matrix}}$, since heating with concentrated hydrochloric acid effected a smooth hydrolysis into acetone, hydrazine hydrochloride, and 2 : 4-diketotetrahydrothiazole, $OC{<}{\begin{matrix}NH{\cdot}CO\\S{-}CH_2\end{matrix}}$. This appears to be a ψ-thiohydantoin derivative of a new type; such derivatives should be easily obtained by this method. This reaction is similar to the one which occurs on heating ethyl chloroacetate with thiocarbamide in alcoholic solution,

$$NH{:}C{<}{\begin{matrix}NH_2\\SH\end{matrix}} + CH_2Cl{\cdot}CO_2Et = NH{:}C{<}{\begin{matrix}NH{\cdot}CO\\S{-}CH_2\end{matrix}},HCl + EtOH,$$

whereby ψ-thiohydantoin hydrochloride results (Mulder, *Ber.*, 1875, **8**, 1264; Claesson, *Ber.*, 1877, **10**, 1352).

Ethyl chloroformate was found to react with the sodium derivative of acetonethiosemicarbazone in benzene suspension. The mixture became hot, sodium chloride separated, carbon dioxide was evolved, and a substance melting at 188—189° was obtained. It has been shown by Dixon (T., 1903, **83**, 550) that thiocarbamide and mono-substituted thiocarbamides react with chloroformates in the heat with evolution of carbon dioxide and formation of the hydrochloride of a ψ-thiocarbamide the sulphur of which is attached to the hydrocarbon residue of the chloroformate,

$$NH{:}C(SH){\cdot}NH_2 + Cl{\cdot}CO_2R = NH{:}C(SR){\cdot}NH_2,HCl + CO_2,$$

since heating with sodium hydroxide solution yields a mercaptan. On this analogy, the substance melting at 188—189° would be $CMe_2{:}N{\cdot}N{:}C(SEt){\cdot}NH_2$; the analytical results and a molecular-weight determination were in agreement with this formula, but it is highly improbable that the ethyl group is attached to sulphur, since we failed to obtain a mercaptan from it; further, the melting point is relatively high (the corresponding *S*-benzyl derivative melts at 51—52°). Possibly the ethyl group is attached to a nitrogen atom, but the constitution of this substance is still under investigation.

The action of acid chlorides on the sodium derivatives of thiosemicarbazones appears to give rise to a mixture of substances which are at present being investigated. The action of *l*-menthoxyacetyl chloride and of methyl *l*-chlorosuccinate on these sodium derivatives, and the action of primary amines on thiosemicarbazones are also being studied.

Experimental.

The acetonetbiosemicarbazone required in these experiments was prepared by heating under reflux 30 grams of thiosemicarbazide with 200 c.c. of 90 per cent. alcohol and 70 c.c. of acetone until solution was effected. On cooling, the thiosemicarbazone separated in the pure state, melting at 178—179°. The yield was 80 per cent. of the theoretical. This method is more convenient than the one described by Freund and Schander (*loc. cit.*).

The *silver* derivative was obtained as a white precipitate by adding an alcoholic solution of acetonethiosemicarbazone to excess of alcoholic silver nitrate solution. It is sensitive to light and very sensitive to organic solvents, and was not obtained in a pure state (Found: Ag = 43·9, 44·0. $C_4H_8N_3SAg$ requires Ag = 45·3 per cent.). It did not react with alkyl haloid in ether or light petroleum; in alcohol or benzene, complete decomposition took place on heating.

The *sodium* derivative was obtained by adding the calculated quantity of sodium ethoxide in alcohol to the thiosemicarbazone dissolved in the minimum quantity of hot alcohol, boiling for five minutes, and then adding to the cold solution three to four times its volume of ether. The sodium derivative (yield, 90—95 per cent. of the theoretical) was collected, washed with ether, and dried in a vacuum over sulphuric acid (Found: Na = 15·30, 15·10. $C_4H_8N_3SNa$ requires Na = 15·03 per cent.). It was a white powder, soluble in alcohol or water, and insoluble in benzene or ether; the aqueous solution reacts alkaline.

Acetone-S-*benzylthiosemicarbazone.*

The calculated quantity of benzyl chloride was added to the sodium derivative of acetonethiosemicarbazone dissolved in the minimum quantity of alcohol and the whole allowed to stand overnight. The mixture was then boiled under reflux for five minutes, the sodium chloride filtered off, and the filtrate evaporated to dryness under reduced pressure at as low a temperature as possible. The resulting pasty mass was pressed on porous porcelain and recrystallised from light petroleum. The substance separated in long, colourless needles melting at 51—52° and was very soluble in alcohol, ether, or benzene (Found: N = 19·14, 19·03; *M* = 217, 225 by the cryoscopic method in benzene. $C_{11}H_{15}N_3S$ requires N = 19·00 per cent.; *M* = 221).

This thio-ether was boiled under reflux with 2*N*-aqueous sodium hydroxide until complete solution was effected (two hours). Ammonia was evolved and on distilling acetone passed over; this was identified by the iodoform test and by conversion into its oxime.

The *solution remaining in the distillation flask* was acidified, extracted with ether, the ethereal solution dried over sodium sulphate, and the ether evaporated. The residual liquid was identified as benzyl mercaptan by its boiling point (194—195°), odour, and solubility in aqueous sodium hydroxide.

Acetone-S-*benzylthiosemicarbazone* reacted very slowly with benzenesulphonyl chloride on shaking with aqueous alkali. Reaction readily occurred in alcoholic solution; the substance was dissolved in alcohol, sodium ethoxide (2 mols.) was added, and then benzenesulphonyl chloride (1 mol.). The mixture was boiled for a few minutes, filtered hot from sodium chloride, and two to three volumes of ether were added to the cold solution. The *sodium* derivative of the sulphonamide separated as a white powder, extremely soluble in water, less soluble in alcohol, and insoluble in ether (Found: S = 16·73, 16·90. $C_{17}H_{18}O_2N_3S_2Na$ requires S = 16·71 per cent.).

S-*Benzylthiosemicarbazide Hydrochloride.*

Acetone-*S*-benzylthiosemicarbazone was warmed at 60° with *N*-hydrochloric acid on the water-bath for twenty minutes. The solution was then evaporated to dryness on the water-bath, acetone distilling off during the evaporation. Addition of dilute sodium carbonate solution to the residue caused the separation of a pasty solid, which was very unstable and could not be obtained in a pure condition. It was dissolved in ether, and a current of dry hydrogen chloride was passed through this solution, which had been previously dried over sodium sulphate. The hydrochloride separated as a white, granular precipitate, which was collected, washed with ether, and dried in a vacuum over sulphuric acid. It was soluble in water and in alcohol, and melted at 124—126° with decomposition (Found: N = 19·00; Cl = 16·00. $C_8H_{11}N_3S,HCl$ requires N = 19·31; Cl = 16·32 per cent.). The *sulphate* was prepared by adding a little concentrated sulphuric acid to an ethereal solution of the impure base and recrystallising the precipitate from alcohol; it separated in small, colourless needles melting at 148° with slight decomposition, and was soluble in water and insoluble in ether [Found: H_2SO_4 = 21·10 as $BaSO_4$. $(C_8H_{11}N_3S)_2,H_2SO_4$ requires H_2SO_4 = 21·30 per cent.].

Benzaldehyde-S-*benzylthiosemicarbazone* was prepared by adding a few drops of benzaldehyde to an aqueous solution of the hydrochloride and shaking. After standing over-night, the substance was collected and recrystallised from alcohol, from which it separated in colourless needles melting at 190° (Found: N = 15·50. $C_{15}H_{15}N_3S$ requires N = 15·61 per cent.).

Action of l-Menthyl Chloroacetate and of Ethyl Chloroacetate on the Sodium Derivative of Acetonethiosemicarbazone.

l-Menthyl chloroacetate and the sodium derivative were heated together in alcoholic solution. Sodium chloride separated and the solution on concentration yielded menthol and a substance melting at 175—176°. It was found that the employment of ethyl chloroacetate instead of *l*-menthyl chloroacetate resulted in the formation of the same substance. Ethyl chloroacetate (1 mol.) was added to a warm alcoholic solution of the sodium derivative (1 mol.), sodium chloride separated at once, and the reaction was completed by boiling on the water-bath until the alkaline reaction had disappeared. The solid which separated on cooling was collected, washed with water, and recrystallised from alcohol, from which it was deposited in colourless plates melting at 175—176°. It was somewhat soluble in hot water, readily soluble in warm aqueous sodium hydroxide, from which it was reprecipitated unchanged on acidification, and readily soluble in hot alcohol or chloroform. The yield was 80 per cent. of the theoretical (Found: N = 24·35, 24·36; M = 158, 162 by the ebullioscopic method in alcohol. $C_6H_9ON_3S$ requires N = 24·54 per cent.; M = 171).

To determine the constitution of this compound, it was hydrolysed by warming with very dilute hydrochloric acid. Acetone, recognised by its odour and by the iodoform test, distilled over, and there was obtained apparently the hydrochloride of a base, which, however, rapidly decomposed, giving a substance insoluble in solvents. A very smooth hydrolysis was effected by boiling the substance with concentrated hydrochloric acid; the solution was evaporated to dryness on the water-bath, and the residue allowed to remain for some time in a vacuum over concentrated sulphuric acid and soda-lime. The crystalline mass was repeatedly extracted with hot chloroform, which, on cooling, deposited 2 : 4-diketotetrahydrothiazole, identified by its melting point (125—126°) and by comparison with a known specimen. The residue insoluble in chloroform was very soluble in water and was identified as hydrazine hydrochloride by reduction of Fehling's solution and by conversion into hydrazine sulphate and into benzalazine.

The substance melting at 175—176° was therefore a ψ-thiohydantoin derivative of the structure $CMe_2{:}N{\cdot}N{:}C{<}\begin{matrix}NH{\cdot}CO\\ S{-\!\!-}CH_2\end{matrix}$.

Action of Ethyl Chloroformate on the Sodium Derivative of Acetonethiosemicarbazone.

Ethyl chloroformate (1 mol.) was added with shaking to the sodium derivative (1 mol.) suspended in a small quantity of dry

benzene. The mixture became sufficiently hot to cause the benzene to boil, and carbon dioxide was evolved. The reaction was completed by boiling for an hour. The product was filtered, washed with water to remove sodium chloride, and recrystallised from alcohol. The substance separated in colourless, lustrous flakes melting at 188—189°, readily soluble in hot acetone, moderately soluble in boiling alcohol, and almost insoluble in benzene or chloroform. It dissolved in hot water and in cold aqueous sodium hydroxide, and slowly dissolved in concentrated hydrochloric acid. The yield was very variable (Found: N = 26·30; S = 20·27, 20·00; C = 45·00; H = 8·06; M = 146, 149 by the ebullioscopic method in acetone. $C_6H_{13}N_3S$ requires N = 26·41; S = 20·12; C = 45·28; H = 8·18 per cent.; M = 159). On heating with $2N$-aqueous sodium hydroxide for two hours, no mercaptan could be detected after acidification.

It was found that if alcohol were used instead of benzene the reaction took a different course. Sodium chloride separated and acetonethiosemicarbazone was formed, the alcohol reacting apparently with the ethyl chloroformate.

In conclusion, we wish to express our thanks to the Governors of this College for a scholarship which has enabled one of us (R. B.) to participate in this investigation. We desire also to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this work.

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C.—*The Essential Oil from* Blumea Malcomii.

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Blumea Malcomii, which is known in Marathi as "*Panjrut*," is a small herb the stem of which is covered with rough wool. It occurs in the western part of the Deccan plateau at elevations above 2000 feet. The herb has a pleasant camphoraceous smell, and it was suggested in 1914 by the then Divisional Forest Officer of Belgaum, Mr. Hodgson, that it might on distillation yield an essential oil. Preliminary experiments made in the field in 1915 by Mr. Puran Singh showed that the herb on distillation in steam yielded about 0·26 per cent. of an oil which resembled caraway-seed oil in smell, but was somewhat milder. During the last growing season (November, 1921) a further quantity of the oil was distilled in a small camp-still at Belgaum, since it was found

that the herb, if kept for any length of time, lost practically all its oil content. The small young herbs were found to give the highest yield of oil, which, in confirmation of previous results, was found to be about 0·25 per cent. calculated on the fresh, green material.

A careful examination of the oil has shown that it consists almost entirely of two ketones, *d*-carvotanacetone (Δ^6-menthen-2-one) and *l*-tetrahydrocarvone (*p*-menthan-2-one), the former forming about 82 per cent. by weight of the oil, and the latter about 16 per cent. The two ketones were readily separated by taking advantage of the fact that, whereas carvotanacetone readily reacted with a neutral solution of sodium sulphite, tetrahydrocarvone did not react with this reagent. The *l*-tetrahydrocarvone was separated from the residual oil by means of its sparingly soluble semicarbazone, since, although it formed a crystalline compound with sodium hydrogen sulphite, this substance was so readily dissociated by water that its use was not found to lead to satisfactory results.

The occurrence in nature of carvotanacetone would not appear to have been previously definitely established. Wallach (*Annalen*, 1894, **279**, 385), who first isolated this ketone from thuja oil, doubted whether it existed preformed in the oil, since he considered that the small quantity present might have been formed from thujone during the process of extraction. The identity of the ketone isolated by means of its sodium sulphite compound from *Blumea Malcomii* with *d*-carvotanacetone was clearly shown by a comparison of its physical properties with those which have been found for carvotanacetone and also by the properties of its derivatives (see Table I).

TABLE I.

*Carvotanacetone.**	d-*Carvotanacetone from* Blumea Malcomii.
B. p. 227–228°/760 *mm.*	227·5°/707 *mm.*
$d^{19°}$ 0·9351	$d^{30°}_{30°}$ 0·9305
$n_D^{19°}$ 1·4832	$n_D^{30°}$ 1·4767
$[\alpha]_D$ +49·5°	$[\alpha]_D^{30°}$ +59·55°
d-Oxime, m. p. 75–77°	77°
d-Semicarbazone, m. p. 173–174°	173–174°
d-Hydroxylamino-oxime, m. p. 95–96°	95–96°
d-Phenylhydrazone, m. p. —	92–93°
d-H_2S deriv., m. p. 222–225°	225–226°

TABLE II.

*Tetrahydrocarvone.**	l-*Tetrahydrocarvone from* Blumea Malcomii.
220–221°	218·5–219°/705 mm.
$d^{20°}$ 0·904	$d^{30°}_{30°}$ 0·9001
$n_D^{20°}$ 1·4554	$n_D^{30°}$ 1·4531
—	$[\alpha]_D^{30°}$ −9·33°
l- 97–99°	*l*- 96–97°
186–188°, 194–195°	194–195°

* Baeyer, *Ber.*, 1893, **26**, 822; 1895, **28**, 1588; 1896, **29**, 37. Wallach, *Annalen*, 1893, **277**, 133; 1894, **279**, 385; 1895, **286**, 102; 1899, **305**, 206; 1900, **312**, 302; 1904, **336**, 37; *Ber.*, 1895, **28**, 1961. Harries, *Ber.*, 1901, **34**, 1928.

The oxidation of carvotanacetone with potassium permanganate was investigated by Semmler (*Ber.*, 1900, **33**, 2454), who obtained pyruvic acid and *iso*propylsuccinic acid. The authors have found that under the experimental conditions used by them (see page 880) acetic acid and β-*iso*propylglutaric acid are the sole products of the reaction. No evidence of the presence of pyruvic acid was obtained; the formation, however, of β-*iso*propylglutaric acid affords definite proof of the constitution of the ketone under investigation.

The presence of tetrahydrocarvone in nature does not appear to have been observed previously, although it has been prepared synthetically both in its racemic and optically active forms by Baeyer and Wallach (*loc. cit.*). The identity of the natural ketone with that prepared synthetically will be clearly seen by reference to Table II above.

From the active ketone, Wallach (*loc. cit.*), besides isomerides of lower melting point, isolated a pure semicarbazone melting at 186—188°, whereas Baeyer (*loc. cit.*) has shown that the semicarbazone of the active ketone melted at 194—195°. In agreement with Wallach, the authors have found that *l*-tetrahydrocarvone on treatment with semicarbazide, gave a mixture of semicarbazones, from which, however, the main fraction was obtained in beautiful needles melting, as stated by Baeyer, at 194—195°. It may be mentioned that Wallach also obtained a small fraction melting at this temperature, but he did not describe the substance in detail. It was not found possible to separate from the more fusible fractions a pure β-semicarbazone, although the absence of any other ketone was established by hydrolysing the crude mixture of semicarbazones and converting the resulting ketone into the oxime, which melted at 96—97°. The formation of a mixture of semicarbazones cannot be regarded as surprising, since tetrahydrocarvone, like menthone, should exist in four active and two racemic forms. A further study of tetrahydrocarvone is therefore contemplated with the object of preparing the optically pure isomerides.

An interesting fact to which attention may be directed is that whereas the carvotanacetone is dextrorotatory, the tetrahydrocarvone is lævorotatory. It would appear probable that the tetrahydrocarvone is formed in the plant by the reduction of the dextrorotatory carvotanacetone, during which process a change in rotation takes place. In confirmation of this view, attention may be directed to the experiments of Vavon (*Compt. rend.*, 1911, **153**, 69), who has shown that when *d*-carvone is reduced with hydrogen in the presence of platinum black, *d*-carvotanacetone is first formed, which on further reduction yields *l*-tetrahydrocarvone

and *l*-tetrahydrocarveol. It would therefore appear to be more correct to call lævorotatory tetrahydrocarvone *d*-tetrahydrocarvone to indicate its relationship to *d*-carvone and *d*-carvotanacetone, but in view of our imperfect knowledge of the stereochemistry of the isomeric tetrahydrocarvones this change may for the present be deferred.

In addition to the two ketones, a trace of a phenol was also isolated together with a mixture of fatty acids and sesquiterpenes, but they were not obtained in sufficient quantity for identification.

EXPERIMENTAL.

The oil used in these experiments was pale brown and had a smell resembling that of caraway-seed oil, but had in addition a distinct smell of peppermint. It had the following constants: $d_{30^\circ}^{30^\circ}$ 0·9296, $n_D^{30^\circ}$ 1·4749, $[\alpha]_D^{30^\circ}$ +46·76°, acid value 0·11, saponification value 22·93, saponification value after acetylation 60·63. The amount of ketone present, as estimated by absorption with neutral sodium sulphite solution, was 82 per cent. by weight, whilst the total ketonic content estimated by means of hydroxylamine (Bennett, *Analyst*, 1909, **34**, 14) was found to be 97 per cent.

In order to determine the constituents present in the oil, it was washed with dilute sodium carbonate solution to remove the free acids, then with a 5 per cent. solution of sodium hydroxide to remove the phenols, and finally it was treated with excess of neutral sodium sulphite solution to extract the ketone. The residual oil was reserved for further investigation.

d-*Carvotanacetone.*

The neutral sodium sulphite solution, which contained the bulk of the oil, was made strongly alkaline with sodium hydroxide solution, the oil which separated dissolved in ether, the ethereal solution dried and evaporated, and the ketone distilled at 100 mm., when almost the whole passed over between 154° and 155°. On redistillation at the ordinary pressure, it boiled constantly at 227·5°/707 mm. The constants of the oil are given in Table I (Found: C = 79·0; H = 10·5. Calc., C = 79·0; H = 10·4 per cent.).

d-*Carvotanacetoxime.*—This substance, which was prepared in the usual manner, crystallised from methyl alcohol in beautiful prisms melting sharply at 77°. In methyl-alcoholic solution it was dextrorotatory, $[\alpha]_D^{30^\circ}$ + 15·3°. Wallach (*loc. cit.*) gives the value $[\alpha]_D$ + 19·2° (Found: C = 72·1; H = 10·1. Calc., C = 71·8; H = 10·2 per cent.).

d-*Carvotanacetone Hydroxylamino-oxime.*—This substance was

prepared by the method used by Read and Smith (T., 1921, **119**, 783) for the preparation of piperitone hydroxylamino-oxime. The crude product was distilled in steam to remove a trace of the oxime and finally purified by crystallisation from ether, when it was obtained in fine needles melting at 95—96°. It crystallised, as stated by Harries (*loc. cit.*), with half a molecule of water of crystallisation (Found : C = 57·1 ; H = 10·3. Calc., C = 57·4 ; H = 10·0 per cent.).

d-*Carvotanacetonesemicarbazone* crystallised from methyl alcohol in glistening rhombohedra melting at 173—174°. In pyridine solution, it was found to be dextrorotatory, $[\alpha]_D^{30^\circ}$ + 89·54°. Wallach (*loc. cit.*) gives the value $[\alpha]_D$ + 114·69° (Found : C = 63·5 ; H = 9·3. Calc., C = 63·1 ; H = 9·1 per cent.).

d-*Carvotanacetonephenylhydrazone*.—This substance, which does not appear to have been described previously, was readily formed when equimolecular proportions of *d*-carvotanacetone and phenylhydrazine were warmed together on the water-bath for a short time in the presence of a little acetic acid. It was purified by crystallisation from alcohol, from which it separated in almost colourless needles melting at 91—92°. In pyridine solution, it was dextrorotatory, $[\alpha]_D^{30^\circ}$ + 93·97° (Found : C = 79·2 ; H = 9·3. $C_{16}H_{22}N_2$ requires C = 79·3 ; H = 9·1 per cent.). *d*-Carvotanacetonephenylhydrazone would appear to be dimorphous, since it was obtained also in fatty plates which melted at the temperature given above. It was found to be extremely unstable and decomposed completely, giving a red oil, when kept for twenty-four hours. It dissolved in dilute sulphuric acid, giving a clear emerald-green solution which on warming clouded and became colourless, the ketone being regenerated. All attempts to convert the hydrazone into the corresponding carbazole derivative were unsuccessful. The *compound* of *d*-carvotanacetone and hydrogen sulphide crystallised from acetic acid in glistening needles melting at 225—226°.

Oxidation of d-*Carvotanacetone*.—The ketone (50 grams) was mixed with dilute sodium hydroxide solution (20 grams of NaOH) and after the addition of ice potassium permanganate solution (5 per cent.) was added, the whole being well stirred, until a permanent pink colour was obtained (approximately 4000 c.c. of the solution of permanganate were required). After filtration, the alkaline solution was concentrated to a small bulk in a current of carbon dioxide, acidified, the acids formed in the oxidation were extracted with ether, and the ether was dried and evaporated. The crude mixture of acids, which smelt strongly of acetic acid, was carefully tested for pyruvic acid with negative results. The mixture of acids was esterified in the usual manner, and the result-

ıg ester, which smelt strongly of ethyl acetate, fractionated under iminished pressure (28 mm.), when almost the whole passed over etween 154° and 155° (yield 50 grams). The acid formed by ydrolysis of the pure ester with alcoholic potassium hydroxide was ıolated in the usual manner, when it was obtained as a crystalline ake. It was purified by crystallisation from water, when it eparated in plates melting at 103—104° (Found: C = 55·3; I = 8·0; M = 175. $C_8H_{14}O_4$ requires C = 55·1; H = 8·0 per ent.; M = 174). This acid evidently consisted of β-*iso*propyl-lutaric acid, which is stated by Howles, Thorpe, and Udall (T., 900, 77, 944) to melt at 100°. The anilic acid was prepared as lescribed by these authors and crystallised from alcohol in lustrous ılates or from benzene, in which it was very sparingly soluble, in osettes of needles melting at 123°, whereas Howles, Thorpe, and Jdall give the melting point as 121° (Found: N = 5·6. Calc., N = 5·6 per cent.).

l-*Tetrahydrocarvone.*

The oil remaining after the removal of the *d*-carvotanacetone with neutral sodium sulphite solution was distilled under diminished pressure (100 mm.), when, after a few drops had passed over below 140°, the main fraction distilled at 147—160°, a further small fraction being obtained which distilled from 160—180°. The fraction boiling between 147° and 160° had a strong smell of peppermint and reacted immediately with semicarbazide. It also formed a compound on shaking for some time with a solution of sodium hydrogen sulphite. This compound, which crystallised in fine needles, was dissociated somewhat readily by water and therefore was unsuitable for isolation of the ketone. The whole of the oil was treated with excess of semicarbazide, and after standing for some days the crystalline semicarbazone which had separated was collected.

For the preparation of the pure ketone the crude semicarbazone (70 grams) was crystallised from a large quantity of alcohol, when a large fraction (50 grams) was obtained in fine needles melting at 192—193°. On further crystallisation from alcohol, the melting point was raised to 194—195°, decomposition taking place slightly above this temperature. *l*-Tetrahydrocarvonesemicarbazone crystallised in long, prismatic needles, and in pyridine solution was found to be optically inactive, although the ketone obtained therefrom was optically active (see Table II) (Found: C = 62·4; H = 9·8. Calc., C = 62·6; H = 9·9 per cent.).

On hydrolysis of the pure semicarbazone with dilute sulphuric acid, the ketone was obtained, which was purified by distillation

in steam and fractionation, first under diminished pressure (100 mm.), when it distilled at 146—148°, and finally by distillation under the ordinary pressure, when it boiled at 218·5—219°/705 mm. The constants of pure *l*-tetrahydrocarvone are given in Table II (Found: C = 78·0; H = 11·4. Calc., C = 77·9; H = 11·7 per cent.).

The more soluble semicarbazones from which the pure *l*-tetrahydrocarvonesemicarbazone had been separated were fractionally precipitated with water. The fractions crystallised, as stated by Wallach (*loc. cit.*), in needles, but a fraction of constant melting point could not be obtained. The absence of any other ketone was proved by the fact that the ketone regenerated from the soluble semicarbazones distilled at 146—148°/100 mm. and yielded an oxime which crystallised immediately and melted at 96—97°.

The oil remaining after the removal of the *l*-tetrahydrocarvone was boiled with excess of alcoholic potassium hydroxide solution to hydrolyse any esters present, and fractionated under diminished pressure (100 mm.), when a small quantity of an oil was obtained which passed over between 160° and 180°. It was pale yellow in colour and evidently consisted of a mixture of sesquiterpenes and sesquiterpene alcohols. It was not obtained in sufficient quantity for purification.

Free Acids.—The sodium carbonate extract of the original oil (see above) was extracted with ether to remove any adherent oil, acidified with dilute sulphuric acid, and distilled in steam, the distillate being collected in two fractions. Both fractions, which had the usual smell of the higher fatty acids, were converted into the silver salts in the usual manner and gave the following results on analysis: Fraction I. Ag = 55·6. $C_4H_7O_2Ag$ requires Ag = 55·4 per cent. Fraction II. Ag = 42·8. $C_8H_{15}O_2Ag$ requires Ag = 43·0 per cent. From these results it would appear that the free acids present consisted of a mixture of butyric or *iso*butyric acid and *n*-octoic acid. The residue remaining in the flask after the removal of the volatile acids consisted of a resin, from which nothing could be separated.

Combined Acids.—The alkaline solution resulting from the hydrolysis of the ketone-free oil with alcoholic potassium hydroxide (see above) was freed from alcohol and acidified with dilute sulphuric acid. The mixture of acids thus obtained (3 grams) was distilled in steam, when a small quantity of an oil passed over. The silver salt contained 49·7 per cent. of silver, and the acid was probably a mixture of the two above-mentioned acids. A considerable quantity of acid was not volatile in steam and was soluble in hot water, from which it separated as a viscid oil. The nature of this acid or mixture

of acids was not elucidated; the silver salt gave Ag = 45·7 per cent.

Phenols.—The sodium hydroxide solution containing the phenols present in the original oil (see above) was saturated with carbon dioxide, and the liberated phenol extracted with ether, the ether dried, and evaporated. The residual oil (yield 0·1 per cent.) gave with ferric chloride a brown coloration. It gave, on treatment with benzoyl chloride, a small quantity of a crystalline benzoyl derivative, which, after crystallisation from alcohol, from which it separated in needles, melted at about 52—53°. It was not obtained in sufficient quantity for analysis.

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CI.—*Preliminary Note on the Interchange of Alcohol Radicles in Esters.*

By AKIRA SHIMOMURA and JULIUS BEREND COHEN.

THE present investigation arose out of an attempt to obtain optically active acids by distilling the methyl or ethyl ester of an inactive (*dl*) acid containing asymmetric carbon with an active alcohol such as *l*-menthol or *l*-borneol.

The method is based on a paper by Purdie and Marshall (T., 1888, **53**, 391), who found that alcohol radicles may be interchanged in esters by treating the ester of one alcohol with a second alcohol in presence of a minute quantity of metallic sodium. Later Cohn (*Monatsh.*, 1900, **21**, 200) and Lapworth and Hann (T., 1902, **81**, 1501) found that ethyl acetoacetate partly exchanges its ethyl group for menthyl by simply heating the former with menthol without the addition of sodium.

Although we failed in our object of producing optically active acids by this method, the results we have obtained by the study of the action of menthol or borneol on a variety of esters in general seem sufficiently interesting to be recorded.

We find that interchange takes place in the case of some esters both with and without sodium, in others only when sodium is present, in others again no interchange occurs under either condition.

The effect of sodium is probably to form the alcoholate with the free alcohol, which then exchanges its radicle for the combined alcohol of the ester. We have been able to show that menthol liberates ethyl alcohol from sodium ethoxide, and we offer as a

provisional explanation, where sodium is used, the following scheme:

$$\text{(I.)}\quad R\cdot C{<}^{O}_{OR'} + R''\cdot ONa \rightarrow R\cdot \underset{OR''}{\overset{ONa}{C}}{-}OR' \rightarrow R\cdot C{<}^{O}_{OR''} + R'\cdot ONa$$

$$\text{(II.)}\quad R'\cdot ONa + R''\cdot OH \rightarrow R'\cdot OH + R''\cdot ONa,$$

where R′ is the inactive and R″ the active alcohol group. That such intermediate additive compounds are formed with sodium ethoxide has been shown by Claisen (*Ber.*, 1887, **20**, 646). Beyond this we are unable at present to offer any explanation of the reaction.

Interchange between menthol and ethyl acetoacetate occurs readily with or without sodium; with the ethyl ester of methylacetoacetic acid it also occurs, but less readily; with the ethyl ester of methylethylacetoacetic acid no interchange can be effected under either condition. Ethyl acetoacetate also undergoes interchange with borneol.

In the case of ethyl oxalate interchange readily takes place, but only in presence of sodium; but under no condition with ethyl malonate or succinate.

Again, interchange occurs with methyl phenylchloroacetate, or methyl phenylacetate, but only if sodium is present; under similar conditions no interchange was observed with methyl phenylbromoacetate.

It occurs also with ethyl benzoate, but again only in presence of sodium, but no change was produced with the methyl ester of either *o*- or *p*-toluic acid and only to a very slight extent in the case of the meta-acid.

EXPERIMENTAL.

The following general method was adopted: a few centigrams of metallic sodium were first dissolved in the menthol (equivalent to the ester used) and about 10 grams of the ester were added. The mixture was heated for several hours either at about 150° or at 80—90° under reduced pressure, according to circumstances. The mixture was then subjected to a careful fractional distillation under diminished pressure.

l-*Menthol and Methyl* (*or Ethyl*) *Phenylacetate.*—Ten grams of ester, about 0·03 gram of sodium, and the equivalent quantity of *l*-menthol were heated at 80—90° for six hours at 10—30 mm. pressure. A very small fraction (less than 1 gram), which distilled at about 180°/8 mm., was collected, and after being subjected to steam distillation to separate any menthol, was extracted with ether and dried over sodium sulphate. The ethereal solution, on evaporation, gave a colourless oil, showing $[\alpha]_D^{17°}$ − 65·3° (c = 6·56,

$l = 2$) in alcoholic solution, and was found to be *l*-menthyl phenylacetate by analysis (Found: C = 78·51; H = 9·51. Calc., C = 78·78; H = 9·55 per cent.).

l-*Menthol and Methyl Phenylchloroacetate*.—When a molecular mixture was heated at 80—90° for four and a half hours at 10—30 mm., no interchange of the groups took place, but the addition of a small quantity of sodium gave a little *l*-menthyl phenylchloroacetate (3·8 grams from 9·5 grams of the methyl ester in one case and 4·6 grams from 18 grams of ester in the other), which distilled at 190—200°/8 mm. and solidified to a crystalline mass. It was obtained in colourless prisms from alcohol, m. p. 38—40°, $[\alpha]_D^{9°} - 80°$ ($c = 1·05$, $l = 2$) in alcoholic solution (Found: Cl = 11·28. Calc., Cl = 11·49 per cent.). It appeared to be identical with the substance obtained directly from *l*-menthol and phenylchloroacetyl chloride (T., 1921, **119**, 1818).

The menthyl ester was hydrolysed with a calculated amount of alcoholic potash (1 c.c. containing 0·016 gram of KOH) at the ordinary temperature, but, after complete separation of the menthol, the phenylchloroacetic acid (m. p. 77—78°) obtained showed no appreciable optical activity.

l-*Menthol and Ethyl Acetoacetate*.—Following the method of Lapworth and Hann (*loc. cit.*), 10 grams of ester and 12 grams of *l*-menthol were heated together at 150° for three and a half hours in a distilling flask; 2·5 grams of ethyl alcohol were condensed during the reaction, and on fractionating the product under diminished pressure 9·9 grams of menthyl acetoacetate (b. p. 153°/12 mm.) were obtained, which crystallised in fine needles (m. p. 32°) either from ether or alcohol by cooling in a freezing mixture. It showed $[\alpha]_D^{11°} - 67·4°$ ($c = 2·67$, $l = 2$) in a freshly prepared alcoholic solution and $[\alpha]_D^{11°} - 69·7°$ on the following day. The anhydrous copper derivative melted at 118°.

A similar experiment was carried out with addition of 0·0430 gram of sodium, but without any improvement in the yield of the menthyl ester.

l-*Menthol and Ethyl Methylacetoacetate*.—Ten grams of the ethyl ester and 11 grams of *l*-menthol were heated together at 140—150° for five hours. The fraction (5·9 grams) which distilled at 143—149°/8 mm. was collected. The menthyl ester boiled at 154—155°/11 mm. and showed $[\alpha]_D^{12°} - 67·7°$ ($c = 2·34$, $l = 2$) in a freshly prepared alcoholic solution and $[\alpha]_D^{12°} - 69·0°$ on the following day (Found: C = 70·40; H = 10·26. $C_{15}H_{26}O_3$ requires C = 70·80; H = 10·33 per cent.).

l-*Menthol and Ethyl Oxalate*.—On distilling the product obtained by heating ethyl oxalate (1 mol.) and menthol (2 mols.) at 150—

180° for seven hours, a very small quantity of a liquid (0·4 gram) came over at about 150°/10 mm., but was not identified.

Seven grams of ethyl oxalate, 14·9 grams of *l*-menthol, and 0·0294 gram of sodium were heated at 70—80° for four and a half hours at 10—30 mm. pressure. The product was separated into three fractions:

(*a*) 85—105° up to 135°/10—12 mm., 16·0 grams,

(*b*) 155—167° up to 185°/10 mm., 2·4 grams,

(*c*) up to 208°/10 mm., 1·2 grams.

(*a*) was unchanged ethyl oxalate and menthol; (*b*) appeared to consist of ethyl menthyl oxalate, but was not further examined; (*c*) solidified to a crystalline mass after standing for eight days at the ordinary temperature. When recrystallised from alcohol, it formed colourless needles, m. p. 68° and $[\alpha]_D^{15°}$ − 100° ($c = 1·00$, $l = 2$) in alcoholic solution, and was identical with menthyl oxalate prepared directly from oxalic acid and menthol in the following way: 5 grams of oxalic acid were first dehydrated and then heated with 12·4 grams of menthol and 0·5 c.c. of concentrated sulphuric acid for five hours. The dark coloured product was extracted with ether, washed first with water, then with dilute sodium hydroxide solution, and finally with water again. The ethereal solution was dried over calcium chloride, and after the ether had been expelled it was fractionated under diminished pressure. The portion (8·2 grams) which distilled at 223—225°/10 mm. was collected. The oil solidified slowly to a crystalline mass and gave colourless prisms on crystallisation from alcohol, m. p. 68° and $[\alpha]_D^{14°}$ − 100° ($c = 1·00$, $l = 2$) in alcoholic solution.

Menthyl oxalate, unlike ordinary alkyl oxalate, does not give oxamide with ammonia, but menthol is split off when it is heated with ammonia at 150° for several hours.

l-*Menthol and Ethyl Benzoate*.—Thirteen grams of ester and 13·5 grams of menthol with a few centigrams of sodium were heated at 80° for four hours at 10—30 mm. pressure. When the product was fractionated under diminished pressure, a portion (15 grams), which boiled chiefly at 171—173°/9 mm., was obtained and solidified slowly to a crystalline mass. It formed large, colourless needles from alcohol and showed m. p. 56° and $[\alpha]_D^{11°}$ − 87·5° ($c = 2·4$, $l = 2$) in alcoholic solution.

It was identical with the *l*-menthyl benzoate prepared directly from menthol and benzoyl chloride. The latter showed m. p. 56° and $[\alpha]_D^{11°}$ − 86·1° ($c = 2·42$, $l = 2$) in the same solvent.

l-*Borneol and Ethyl Acetoacetate*.—Ten grams of ethyl acetoacetate and 11·7 grams of *l*-borneol were heated at 140—150° for three hours; 2·1 grams of alcohol were condensed during the

reaction. When the product was fractionated under diminished pressure, a portion (12 grams), which boiled at 140—150°/10 mm., was obtained. On redistilling, *l*-bornyl acetoacetate came over as a colourless, mobile liquid, b. p. 150—153°/11 mm. and $[\alpha]_D^{12°} - 34{\cdot}2°$ ($c = 2{\cdot}72$, $l = 2$) in alcoholic solution (Found: C = 70·14; H = 9·29. $C_{14}H_{22}O_3$ requires C = 70·54; H = 9·31 per cent.).

The copper derivative formed pale green microscopic needles and melted toward 212° with decomposition.

l-*Menthol and Sodium Ethoxide*.—When a mixture of anhydrous sodium ethoxide and menthol was heated at 150—160° in an atmosphere of hydrogen, some ethyl alcohol distilled, which boiled at 78° and gave the iodoform reaction.

The following table contains a summary of our results:

Ester.	With sodium.	Without sodium.
With l-menthol.		
Ethyl acetate	−	−
Ethyl bromoacetate		−
Ethyl α-cyanopropionate	−	−
Methyl phenylacetate	+ (small)	
Ethyl ,,	+ (,,)	
Methyl phenylchloroacetate	+	−
Methyl phenylbromoacetate	−	
Methyl α-bromo-β-phenylpropionate	−	
Ethyl acetoacetate	+	+
Ethyl methylacetoacetate		+
Ethyl methylethylacetoacetate	−	
Ethyl oxalate	+	−
Ethyl malonate	−	
Ethyl succinate	−	
Ethyl benzoate	+	−
Methyl *o*-toluate	−	
Methyl *m*- ,,	+ (very small)	
Methyl *p*- ,,	−	
With l-borneol.		
Ethyl acetoacetate		+
Ethyl methylethylacetoacetate	−	
Methyl phenylchloroacetate	−	
With l-amyl alcohol.		
Ethyl methylethylacetoacetate	−	

+ indicates the interchange of the groups.
− indicates no reaction.

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CII.—*The Surface Tension of Mixtures of Alcohol and Water at 25°.*

By LOUIS LEIGHTON BIRCUMSHAW.

IN the course of some experiments on the transition of certain compounds from the colloidal to the crystalloidal state, it was necessary to know the surface tension of mixtures of water and ethyl alcohol of all compositions from pure water to pure alcohol. The surface tension of these liquids and their mixtures has been determined by Firth (T., 1920, **33**, 268) by the drop-weight method, assuming that the surface tension was directly proportional to the weight of the drop for a given diameter of tip.

The work of Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499), which was published in America just before Firth's paper appeared, has, however, proved that this proportionality can be maintained only as a first approximation, and that for the purpose of obtaining exact results the simple formula of Tate must be modified by the introduction of a factor ϕ, so that the relationship becomes

$$W = mg = 2\pi r\gamma\phi,$$

where W is the weight of the drop which falls from a tip of radius r, and γ is the surface tension of the liquid. The magnitude of the correction was determined in the cases of water and of benzene by measuring accurately the surface tension by the capillary tube method, and then determining the weight of the drop which fell from a series of twenty-eight tips of different radius, the radii of which ranged from 1 cm. down to 0·1 cm. They found that the correction ϕ varied in a somewhat complex manner with the ratio of the radius of the tip r to the linear dimensions of the drop, as expressed, for instance, by the cube root of its volume v, but that for equal values of $r/v^{\frac{1}{3}}$ it was independent of the nature of the liquid, and of the material of which the tip was made, whether of glass or of metal. They showed further that the value of the correction ϕ is practically constant when $r/v^{\frac{1}{3}}$ lies between 0·76 and 0·95, and recommend that tips of these dimensions should always be used in measurements of surface tension by the drop-weight method.

In view of the American measurements, it is clear that the tip used by Firth, which had a diameter of 0·35 cm., was too small to give accurate results, the ratio of $r/v^{\frac{1}{3}}$ being 0·40 for water and 0·55 for alcohol * in these experiments instead of 0·76 to 0·95 as recommended by Harkins and Brown. Since Firth calibrated his apparatus with water, his values for the surface tension may be assumed to be correct at this end of the curve; but as the proportion of alcohol is increased they are subject to an error which (if no error of the opposite sign were present) would increase progressively to a maximum of about 6 per cent. in the case of pure alcohol. In the experiments described below, the ratio $r/v^{\frac{1}{3}}$ ranged from 0·73 in the case of water to 1·00 in the case of alcohol, thus conforming with the recommendations of Harkins and Brown as closely as is possible if one tip is to be used for the whole series.

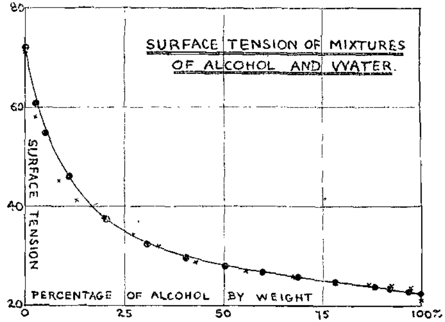
The influence of the time of formation on the weight of the drop was also investigated by Harkins and Brown, who found that six minutes must be allowed for the weight of the drop to become constant, as compared with about seven seconds in the experiments of Firth. If this time were actually allowed, the period required to

* Calculated from the formula $mg = 2\pi r\gamma$.

collect say thirty drops in the case of each determination of a long series would become enormous. Harkins and Brown got over this difficulty by pulling the drop out to a point where it was almost completely formed and then forming the last fraction very slowly. In this way they were able to draw more than thirty drops in thirty minutes without altering the normal weight of the drop. This method was also adopted in the experiments described below.

The differences between the measurements now put forward and the earlier measurements of Firth can be seen by reference to Fig. 1, where Firth's values are indicated by crosses. From this

Fig. 1.



it appears that instead of increasing progressively with the proportion of alcohol, the differences between the two series of observations are distributed somewhat erratically, being relatively small at the two ends and in the centre of the curve, but increasing to nearly 8 per cent. between 5 and 15 per cent. of alcohol.

The new measurements fail to show the sudden bend in the curve which Firth recorded at a point corresponding with the composition of the *minimum-boiling mixture* of alcohol and water. Since this kink does not appear in the measurements made at 15° by Weinstein by the *method of capillary rise*, nor in the *measurements* of Pederson by the method of ripples, it is difficult to believe that it has any real existence.

Experimental.

The apparatus was a slightly modified form of that used by Harkins and Brown. Thus, for the subsequent work on colloids

it was inadvisable to use tips of Monel metal; these were therefore replaced by a glass tube and tip, the latter being ground perfectly flat and made parallel to the platform carrying the spirit levels, as in the American apparatus. The glass tube, in the usual U-form, was fixed through two holes in the top of the box with a little wax, the trace of wax on the inside being covered with a little "punimakos" cement. The two weighing-bottles, each with a ground-glass neck, were held in position against two thin rubber washers stuck on the top of the box by a spring attached to a vertical support, which was also screwed into the top of the box. The diameter of the tip was measured on a travelling microscope in three different directions and found to be 0·6432, 0·6433, and 0·6433 cm., each of these figures being the mean of a number of determinations.

In making a determination, the supply bottle was filled with liquid to the correct level, the two weighing-bottles were fixed in position by the springs, the box was screwed on, and the apparatus immersed in a thermostat at 25 ± 0·01° for twenty to thirty minutes. The platform on the top of the apparatus was then levelled and a drop quickly blown out (one to three seconds) and held on the tip for exactly one minute (timed by a stop-watch) and then allowed to drop off. The drops were blown over by gentle pressure from the mouth through a fine piece of rubber connected with the metal tube passing into the top of the supply cup, a large U-tube filled with calcium chloride and another filled with soda-lime being inserted between the mouth and the metal tube. It was found that perfect control could be exercised over the drop in this way, much more so than by any mechanical contrivance such as the mercury tube recommended by Harkins, but not used by him in his later work. In all cases thirty drops were blown over and the first drop was allowed to hang for five minutes in order to saturate the space in the bottle with vapour, so that all succeeding drops fell into their saturated vapour. The box was then removed from the thermostat and taken off. The bottle containing the drops was cooled for three minutes in ice-cold water, taken off, stoppered, and weighed after standing in the balance case for fifteen minutes. A correction was made for the weight of the vapour required to saturate the space in the bottle. This amounted to 0·0009 gram in the case of pure water and 0·0054 gram in the case of alcohol.

The surface tension was calculated from the corrected weight of the drop by means of the formula $W = 2\pi r\gamma\phi$, using the values of ϕ given by Harkins and Brown for various values of $r/v^{\frac{1}{3}}$. Although the values of $r/v^{\frac{1}{3}}$ fell almost wholly on the flat part of their curve, a separate correction for ϕ was made in every case.

The alcohol was purified by heating rectified spirit under reflux

over lime and fractionating; it contained 97·00 per cent. of alcohol by weight and the proportion of water which it contained was allowed for in making up the various mixtures. The pure alcohol used in the last determination was prepared by boiling this with an excess of calcium for six days, distilling in an apparatus which had been dried by a current of warm air, and collecting in a receiver sealed from the air. Its density was $d_{4°}^{25°}$ 0·78494, the value given by the Bureau of Standards (*Bull.*, vol. 9, No. 3) being 0·78506.

The results of the experiments are given in Table I and are shown graphically in Fig. 1.

TABLE I.

Surface tension of alcohol–water mixtures at 25°.

Alcohol (percentage by weight).	$d_{4°}^{25°}$	Weight of drop (corrected).	$r/v^{\frac{1}{3}}$.	ϕ.	Surface tension. Dynes/cm.
0·0	0·99707	0·09200	0·72	1·6476	72·20
2·72	0·99212	0·07549	0·76	1·6596	60·79
5·21	0·98784	0·06796	0·78	1·6632	54·87
11·10	0·97834	0·05685	0·82	1·6679	46·03
20·50	0·96569	0·04636	0·88	1·6680	37·53
30·47	0·94983	0·04001	0·93	1·6612	32·25
40·00	0·93176	0·03679	0·94	1·6592	29·63
50·22	0·90958	0·03468	0·95	1·6572	27·89
59·58	0·88801	0·03327	0·96	1·6537	26·71
68·94	0·86623	0·03206	0·96	1·6537	25·71
77·98	0·84346	0·03084	0·97	1·6502	24·73
87·92	0·81900	0·02952	0·97	1·6502	23·64
92·10	0·80782	0·02895	0·97	1·6502	23·18
97·00	0·79394	0·02813	0·98	1·6467	22·49
100·00	0·78494	0·02755	0·98	1·6467	22·03

Each determination in the above table is the mean of at least two experiments and the results are considered to be accurate within 0·25 per cent. The value for water agrees very well with that given by Harkins (*J. Amer. Chem. Soc.*, 1917, **39**, 354), namely, 72·05.

Summary.

1. The surface tension of mixtures of water and ethyl alcohol, from pure water to pure alcohol, has been determined at 25°.

2. The sharp point of inflexion at a concentration of 4·47 per cent. of water recorded by Firth has not been observed.

The author desires to express his gratitude to Professor T. M. Lowry, F.R.S., for much valuable advice during the course of these experiments; and to the Department of Scientific and Industrial Research for a grant which has enabled this work to be done.

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CIII.—*The Labile Nature of the Halogen Atom' in Organic Compounds. Part I. Titanium Reductions of Substituted Nitroparaffins.*

By THOMAS HENDERSON and ALEXANDER KILLEN MACBETH.

THE reduction of substituted nitroform and of the halogen derivatives of other nitromethanes has already been studied by various workers (Baillie, Macbeth, and Maxwell, T., 1920, **117**, 880; Macbeth and Pratt, T., 1921, **119**, 1356). In previous work the effect of alkaline reducing agents was examined; in this paper the results of titanium reductions are described. The effect of acid solutions of titanium salts on nitro-compounds has already been extensively investigated by Knecht and Hibbert, and their results are summarised in their monograph ("New Methods in Volumetric Analysis"). Up to the present, however, no great amount of attention seems to have been directed to the aliphatic nitro-compounds, and in view of the interesting results obtained with alkaline agents it seemed desirable to carry out a series of titanium estimations.

The simple aliphatic nitro-compounds, such as nitromethane, are quantitatively reduced by acid solutions of titanous chloride, a quantity equivalent to six atoms of hydrogen being required by each nitro-group. The introduction of halogen atoms into the nitromethane molecule does not interfere with the normal course of the reduction, for monobromo- and dibromo-nitromethane each require an amount equivalent to six atoms of hydrogen for the gram-molecular quantity, and dibromodinitromethane requires twice this quantity for the reduction of its two nitro-groups. Substances such as chloropicrin also behave normally.

When tetranitromethane was examined, it was found that the gram-molecular quantity required only eighteen equivalents for its reduction instead of the twenty-four equivalents necessary for the complete reduction of the four nitro-groups to amino-groups. It is evident, therefore, that the first result of reduction in this case is the removal of the labile nitro-group, an effect which has been established in the study of the action of alkaline reducing agents (*loc. cit.*). Thereafter the reduction proceeds, guanidine being ultimately produced. Eighteen equivalents are necessary for the reaction, as is seen from the following equation:

$$C(NO_2)_4 + 9H_2 = (NH_2)_2C{:}NH + HNO_2 + 6H_2O.$$

The nitrous acid split off in the initial reduction is evidently not further acted on by the titanium, a fact which is in agreement with

the results obtained by Knecht and Hibbert, who showed that nitric acid in dilute solution was not reduced beyond the nitric oxide stage.

Chlorotrinitromethane and bromotrinitromethane are also found to require an amount of titanous chloride equivalent to eighteen atoms of hydrogen per gram-molecular quantity. The reaction in these cases is parallel to that just described, and the reaction may be expressed by the general equation:

$$R{\cdot}C(NO_2)_3 + 9H_2 = (NH_2)_2C{:}NH + HR + 6H_2O,$$

where R represents Cl, Br, or NO_2.

In seeking a satisfactory explanation of the effects observed when substituted nitroform and the halogen derivatives of nitromethane are treated with different reducing agents, it is necessary to compare the results obtained in the several cases. The principal reducing agents that have been employed are potassium ferrocyanide, hydrazine, alkaline solutions of potassium sulphite, arsenious acid, etc., and acid solutions of titanous chloride. Potassium hydroxide itself might also be regarded as a reducing agent. With titanium alone of these reagents is the nitro-group attacked. All these reductions remove one of the nitro-groups from tetranitromethane, with the formation of nitroform and nitrous acid or its salts. The nitro-groups of nitroform are further reduced by titanous chloride solutions. Bromo- and chloro-trinitromethane may be classed as behaving in an exactly similar way.

Chattaway and Harrison (T., 1916, **109**, 171) pointed out that tetranitromethane and bromonitroform were reduced by aqueous solutions of potassium ferrocyanide according to the equation:

$$R{\cdot}C(NO_2)_3 + 2K_4Fe(CN)_6 = (NO_2)_3CK + KR + 2K_3Fe(CN)_6,$$

where R represents either Br or NO_2. Chloropicrin and bromopicrin were not attacked by the reagent, even after a treatment extending over several weeks.

The results of the reduction experiments may be summarised for convenience in considering the different cases.

Tetranitromethane.—One nitro-group is readily removed by titanous chloride, hydrazine, potassium ferrocyanide, potassium sulphite, etc. Titanous chloride further reduces to guanidine the nitroform initially produced. Potassium hydroxide also removes one nitro-group, giving the *aci*-potassium salt of nitroform.

Chlorotrinitromethane and Bromotrinitromethane.—The halogen atom is readily removed by alkaline reducing agents and by potassium ferrocyanide. Titanous chloride also splits off the halogen atom, and then reduces the nitro-groups, guanidine being produced.

Dibromodinitromethane.—Hydrazine, potassium ferrocyanide, or potassium hydroxide removes one of the bromine atoms. Titanous chloride reduces the nitro-groups, but leaves the halogen unattacked.

Chloropicrin.—Hydrazine removes one of the chlorine atoms very slowly in the cold. Potassium ferrocyanide is without action. Titanous chloride reduces the nitro-group, but leaves the halogen unattacked.

Monobromo- and Dibromo-nitromethane.—Titanous chloride reduces the nitro-group, but does not remove the halogen. Hydrazine or potassium ferrocyanide is without action.

Chattaway and Harrison (*loc. cit.*), in seeking to explain the results of reduction with potassium ferrocyanide, based their suggestions on the relative dimensions of the spaces occupied by the methane carbon atoms and the attached groups. In the case of tetranitromethane and bromotrinitromethane, it is supposed that these spaces are such as to admit of only three nitro-groups approaching sufficiently near to the centre of attraction of the carbon atom for the maximum attractive force to be exerted which keeps them firmly attached. A fourth group or atom attracted by the carbon, if occupying sufficient space and of suitable configuration, would alter somewhat the relative positions of the groups around the central carbon atom and force them to a greater distance from the centre of attraction, where they would be less firmly held. As a consequence, one might be more or less easily detached by a suitable reagent. Such reagents would, however, not be able to bring about interaction if the spaces occupied by the attached groups or atoms were smaller and these were consequently nearer the centre of attraction and more firmly held. Chattaway and Harrison suggest that the latter condition is apparently present in chloropicrin and bromopicrin, and these are consequently unacted on by potassium ferrocyanide. This view does not commend itself to us, for it does not indicate why the bromine atom should he removed in preference to a nitro-group in the reduction of bromotrinitromethane.

During the past few years investigations of substitution problems in the aromatic series have shown that the position taken up by the substituents is dependent on the nature of the atoms or groups already present in the molecule; and it has heen pointed out that the constitution of the product is determined by a certain effect on alternate atoms in a chain (Prins, *Chem. Weekblad*, 1918, **15**, 571; Vorländer, *Ber.*, 1919, **52**, [*B*], 263). Lapworth (*Rep. Brit. Assoc.*, Bournemouth meeting, Sect. B) has also applied the principle of alternate polarities to explain, and frequently to predict, the direction of chemical changes. The different atoms in a chain are

labelled + and —, elements of recognised polarity being used as starting points (for example, $\overset{-}{O}$, $\overset{-}{Cl}$, $\overset{+}{H}$, $\overset{+}{Na}$, etc.). Lapworth's views originally had an electrical basis, but ionisation was neither assumed nor excluded. Robinson has also applied his theory of the conjugation of partial valencies to a wide range of problems, with striking results (T., 1917, **111**, 964; 1918, **113**, 640; *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4. See also *Ann. Reps.*, 1919, **16**, 87). In this theory also, the alternate effect is brought out, and the system of + — marking of alternate atoms is adopted.

These ideas may be applied to the cases of the halogen-substituted nitromethanes to account for the characteristic reactions observed. Furthermore, when examined from this point of view, it can be shown that *the labile nature of the halogen atom in these compounds* is only a particular case of a much wider phenomenon, for these substances may be correlated with compounds such as acetobromoamide, bromoacetoacetic ester, chloro- and bromo-sulphonamides, derivatives of bromomalonic acid, and other compounds of various types. The application of the views may best be introduced by examining the behaviour of bromotrinitromethane with potassium hydroxide. Starting with the oxygen atoms of recognised polarity, it is seen that the total effect carried to the bromine through alternate atoms in the chain gives it an overwhelming positive charge. In contact with potassium hydroxide, therefore, the bromine reacts with the negative hydroxyl group, giving the potassium salt of nitroform and hypobromous acid, the latter being converted into potassium bromate. Similar results are also obtained with chlorotrinitromethane (Macbeth and Pratt, *loc. cit.*).

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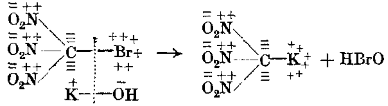


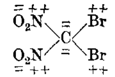
In the above formula for the potassium salt of nitroform, it is seen that owing to the influence of the alternate effect there is a strong positive charge superimposed on the ordinary positive polarity of the potassium atom. This accumulation is probably the force which makes this constitution so unstable that the

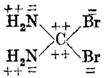
* The negative and positive signs are employed merely to indicate the polarity of the different atoms and are not intended to represent any definite electronic charge; thus the oxygen atom is marked with one minus, and the hydrogen atom is shown with one positive sign.

potassium salt always exists in the aci-form, in which the positive polarity of the potassium is taken up by the negative oxygen atoms.

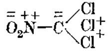
The induced positiveness of the halogen also explains its ready removal by other reducing agents, such as hydrazine and potassium ferrocyanide. Similar reasoning may be applied to account for the analogous results obtained with tetranitromethane. In these cases the reducing agent does not attack the nitro-groups, but with titanous chloride these also are reduced. It must therefore be supposed that the first action of this reagent is to remove the $\overset{+}{Br}$, $\overset{+}{Cl}$, or the $\overset{+}{NO_2}$. Such an assumption seems warranted in the light of the overwhelmingly positive nature of these atoms.

The results obtained with dibromodinitromethane and chloropicrin may next be examined. The former substance is rapidly reduced by hydrazine at the ordinary temperature, one of the bromine atoms being removed. Potassium hydroxide also removes one of the bromine atoms with the formation of potassium bromate and the potassium salt of monobromodinitromethane (Losanitsch, *Ber.*, 1882, **15**, 472). The second bromine atom may be removed by heating with alkaline reducing agents, such as arsenious oxide and potassium hydroxide (Duden, *Ber.*, 1893, **26**, 3004). On the other hand, titanous chloride reduces the nitro-groups, but no removal of bromine occurs. Examining the formula of the substance from the point of view of the alternate effect, it will be noticed that the induced positiveness of the bromine is in this case due to two nitro-groups instead of three as in the preceding cases; and further, this positiveness is distributed between two bromine atoms. When the normal electro-negative nature of the halogen atoms is considered, it will be seen that the net effect of the alternate polarities is to endow the bromine with a slightly positive nature; and it is improbable that such bromine would be reduced by titanous chloride in preference to the nitro-groups. With agents which do not attack the nitro-group, however, the positive nature of the bromine asserts itself, and so it is readily reduced by hydrazine. From this it follows that dibromodinitromethane should be reduced by potassium ferrocyanide; and such is found to be the case. It is not surprising to find that the halogen in dibromodinitromethane is not eliminated in the titanium reduction. In this case the reducing agent has its choice of two points of attack, the nitro-group and the halogen atom; and it is not unreasonable to suppose that the nitro-group offers the greater inducement: dibromodiaminomethane is accordingly produced, and in this the halogen is of a negative type, and therefore the lability connected with the positive bromine disappears.





Since there is only one nitro-group in chloropicrin, the alternate effect results in an induced positiveness on the chlorine atom of smaller degree than that in the case just considered. Moreover, this effect is distributed over the three chlorine atoms and the net effect must therefore be regarded as very small.



It is not surprising to find that such a weakly positive halogen is unattacked by a neutral reducing agent like potassium ferrocyanide, and is but slowly reduced by a strong alkaline reagent like hydrazine. The reduction of the nitro-group without any removal of the halogen by titanous chloride is in perfect agreement with this conception of a weakly positive chlorine.

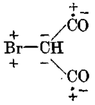
The alternate effect may also be applied to the other well-known cases in which a labile halogen occurs. Kurt Meyer (*Annalen*, 1911, **380**, 212) studied the reduction of certain bromo-ketones by hydriodic acid, and made the reaction the basis of a quantitative estimation of such compounds. The enolic form of ethyl acetoacetate reacts readily with bromine to form a bromo-derivative :

$$-C(OH){:}CH\cdot \xrightarrow{Br_2} \cdot CBr(OH)\cdot CHBr\cdot \longrightarrow \cdot CO\cdot CHBr\cdot + HBr.$$

An alcoholic solution of the bromo-ketone, when treated with potassium iodide and concentrated hydrochloric acid, liberates iodine quantitatively, the bromo-ketone being reduced :

$$\cdot CO\cdot CHBr\cdot + 2HI \longrightarrow \cdot CO\cdot CH_2\cdot + HBr + I_2.$$

A large number of ketones of this type have been studied (*Ber.*, 1911, **44**, 2718, 2725; 1912, **45**, 2843) and examination of their structure shows that they all contain the system ·CO·CHBr·CO·. If this structure is examined from the point of view adopted in the previous cases, it is seen that in such substances the bromine atom has a strong induced positiveness.



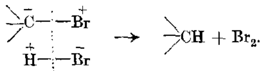
Whiteley and her collaborators have observed that the bromomalonic esters and bromomalonamides are readily reduced by hydriodic acid at the ordinary temperature (P., 1908, **24**, 288; T., 1921, **119**, 359). These substances contain the complex $\cdot CO\cdot CHBr\cdot CO\cdot$ or $\cdot CO\cdot CBr_2\cdot CO\cdot$, and iodine is liberated according to the equations:

$$>CHBr + 2HI = >CH_2 + HBr + I_2.$$

$$>CBr_2 + 4HI = >CH_2 + 2HBr + 2I_2.$$

It is evident that all these cases are further examples of the lability of the bromine atom which has acquired a positiveness through the alternate effect. The system present in the compounds is similar to that dealt with when considering Meyer's results.

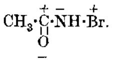
Bromination by compounds of the types considered above is a necessary consequence of the foregoing views, especially if a halogen acid is present:

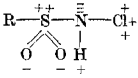


In support of this it has been found that when bromotrinitromethane is shaken with an aqueous solution of phenol containing a little hydrobromic acid, bromination of the phenol takes place with the formation of tribromophenol and nitroform. Supporting examples may be drawn from the work of other observers. Whiteley and her collaborators have pointed out (*loc. cit.*) that when dibromomalon-2 : 4-dibromoanilide is heated with hydrochloric acid in a sealed tube at 120°, hydrolysis occurs and tribromoaniline is formed instead of 2 : 4-dibromoaniline, the production of which would be expected if hydrolysis only took place. Tribromoaniline is also produced when a mixture of dibromomalondiethylamide and 2 : 4-dibromoaniline is similarly treated. These cases are parallel to the bromination of phenol by bromonitroform, the dibromomalonic acid produced by hydrolysis evidently breaking down to the monobromo-acid or to malonic acid itself.

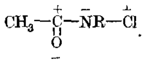
The nitrogen halogen compounds have long been notorious for the ease with which the halogen atom may be removed. This behaviour is also in perfect agreement with the cases we have already quoted, and a few striking examples may be referred to. Wohl (*Ber.*, 1919, **52**, [*B*], 51) pointed out a novel property of acetobromoamide and showed that the substance acted as a brominating agent, even in the absence of hydrobromic acid. Its action on a large number of substances was studied, phenol, for example, being converted into *p*-bromophenol. From the results

t appears that the reaction consists in a direct interchange of ydrogen and bromine between the two molecules concerned. ıcetobromoamide falls into line with the other substances conaining a labile bromine atom, as the halogen is of a positive nature formula A) :

(A.) 

 (B.)

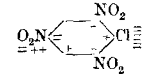
The behaviour of the chloro- and bromo-sulphonamides examined y Chattaway (T., 1905, **87**, 145; *Chem. News*, 1908, **98**, 285) is lso in good agreement with the views we have put forward. These ubstances are readily reduced by hydriodic acid, the reaction eing quantitative and furnishing an effective method of estimation. n formula B it is seen that the halogen in these substances is trongly positive on account of the polarity of the oxygen atoms nd the alternate effect. The lability of the halogen atom attached o nitrogen is further exemplified in the behaviour of *N*-chlorocetanilide and analogous substances. These compounds are so asily reduced that ammonia readily attacks them, with the volution of nitrogen and the formation of the parent acetanilide Short, T., 1921, **119**, 1445). The halogen in these compounds lso is of a positive character :

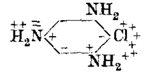


'he application of the alternate effect throws light on many other haracteristic properties of the nitroparaffins. For example, it nay be pointed out that the bromination of the nitroparaffins falls nto line with the work of Lapworth on the bromination of ketones T., 1904, **85**, 30; see also Robinson and Robinson, T., 1917, **111**, 64). It is found that in the case of the lower nitroparaffins the arent substances are not easily brominated, but bromination of he potassium or other salts readily takes place (Scholl, *Ber.*, 1896, 9, 1824; Tscherniac, *ibid.*, 1897, **39**, 2588). These salts have he *aci*-structure and therefore correspond with the enolic modiication of the ketones. Nitroform in acid solution is directly rominated (Macbeth and Pratt, *loc. cit.*). But this is to be xpected, since in the presence of water nitroform itself exists in he *aci*-form (Hedley, *Ber.*, 1908, **41**, 1195).

In a previous paper dealing with the action of hydrazine it was ointed out by one of us that "a certain parallel may be drawn etween the behaviour of the polynitro-aliphatic compounds and

the polynitro-aromatic substances, especially those in which the ortho-para-influence of the nitro-groups exists; in neither does reduction of the nitro-group to an amino-group occur, but in both replacements take place." Too much stress, however, must not be laid on this parallel, as aromatic and aliphatic substances are compounds of very different type. Thus in picryl chloride, for example, it is evident that the chlorine is of a negative nature on account of the alternate effect due to the polarity of the oxygen atoms (formula C):

(C.) 

 (D.)

The distinction in chemical nature is well exemplified by the action of hydrazine (Purgotti, *Gazzetta*, 1894, **24**, i, 112). There is no reduction, with the evolution of nitrogen, such as occurs with chlorotrinitromethane, but instead there is a direct removal of the chlorine atom with the formation of picryl hydrazide and hydrochloric acid. Giua (*Gazzetta*, 1919, **49**, ii, 146, 152, 166) has also shown that the action of hydrazine on the large number of aromatic trinitro-compounds which he examined resulted in the direct removal of the labile nitro-group with the formation of substituted hydrazines. In the titanous chloride reduction of picryl chloride twenty equivalents are required for the complete reduction of the molecular quantity. From this it would appear that the chlorine atom is involved in the reduction and is split off in a way similar to that occurring in the case of chloronitroform. This is at first sight contradictory, but inspection shows that it is quite in agreement with the other results if the reaction takes the course picryl chloride ⟶ chlorotriaminobenzene ⟶ triaminobenzene: for in the triamino-compound the halogen would be strongly positive, and therefore come into line with the other cases (formula D).

Further study of the reduction of picryl chloride is necessary to establish this point, and it is hoped to undertake such work.

From the above considerations it seems clear that the halogen-substituted nitroparaffins are no longer to be regarded as an isolated class, since, when considered from the point of view of the alternate effect in a chain, their chief reactions may be correlated with the chemical properties of substances of a very diverse type. This effect may be of an electrical nature or may not: it may involve some kind of partial ionisation or may be unconnected with this. Whatever the precise nature of the effect may be, it must at least be conceded that there are strong grounds for accepting the existence of some such force in the molecule, since the application of the view

is so fruitful in explaining chemical changes over a very wide field, and has proved trustworthy in predicting the course of many reactions.

EXPERIMENTAL.

The titanium solutions employed in the reductions were prepared by boiling 300 c.c. of commercial titanous chloride (15 per cent. solution) with 500 c.c. of concentrated hydrochloric acid for a few minutes. The resulting solution was diluted to about three litres with water and transferred to a storage apparatus of the usual type. The solution was periodically standardised with methylene-blue and potassium chlorate.

In the estimations, an excess of the titanous chloride solution and 10 c.c. of an alcoholic solution of the nitro-compound were boiled gently under reflux for about half an hour, a slow stream of carbon dioxide being passed during the entire reduction. The solution was then cooled and diluted to 500 c.c. and an aliquot portion titrated against a standardised solution of ferric iron to estimate the excess of titanous chloride. The results quoted in the cases below are the average values obtained in a number of experiments.

Dibromonitromethane was prepared by Scholl's method (*Ber.*, 1896, **29**, 1825). Ten c.c. of a solution (0·9156 gram in 100 c.c. of alcohol), treated with 100 c.c. of titanous chloride solution (21,900 c.c. equivalent to 2 grams of hydrogen), oxidised 27·6 c.c. Therefore the gram-molecular quantity requires the equivalent of 6·032 grams of hydrogen. The nitro-group only is attacked, according to the equation:

$$CHBr_2 \cdot NO_2 + 3H_2 = CHBr_2 \cdot NH_2 + 2H_2O.$$

Monobromonitromethane was prepared by Scholl's method (*loc. cit.*). Ten c.c. of a solution (2·9042 grams in 100 c.c. of alcohol), added to 120 c.c. of titanous chloride solution (16,600 c.c. equivalent to 2 grams of hydrogen), oxidised 96·22 c.c., representing 5·72, or approximately 6 grams of hydrogen for complete reduction of the gram-molecular quantity.

Nitromethane.—Ten c.c. of a solution (2·089 grams in 100 c.c. of alcohol), added to 200 c.c. of titanous chloride (16,166 c.c. = 2 grams of hydrogen) and boiled for twenty minutes, oxidised 160 c.c.; so the gram-molecular quantity requires 5·78 (6 approximately) grams of hydrogen for complete reduction. In the reduction of nitromethane and its monobromo-derivative, no condenser was attached, but on account of the slightly low values obtained this modification was introduced in all other cases.

Dibromodinitromethane was prepared from tribromoaniline (Losanitch, *Ber.*, 1882, **15**, 472). 0·2588 Gram in 10 c.c. of alcohol required 94 c.c. of titanous chloride (16,546 c.c. = 2 grams of hydrogen) for reduction. The molecular quantity therefore requires 11·6 (approximately 12) grams of hydrogen, and it is evident that the nitro-groups only are attacked in the reduction and there is no removal of the halogen such as occurs with hydrazine or potassium ferrocyanide.

Tetranitromethane.—This substance was prepared in the usual way and carefully purified by repeated freezing. 0·1936 Gram in 10 c.c. of alcohol required 143 c.c. of titanous chloride (16,166 c.c. = 2 grams of hydrogen) for complete reduction. The gram-molecular quantity therefore requires 17·9 (approximately 18) grams of hydrogen. It is clear from this result that the four nitro-groups are not fully reduced, as this would require 24 grams of hydrogen. The reaction evidently takes place as formulated on page 892.

Chlorotrinitromethane.—This was prepared according to the method described by Macbeth and Pratt (T., 1921, **119**, 354). 0·26462 Gram in 10 c.c. of alcohol required 216 c.c. of titanous chloride (16,546 c.c. = 2 grams of hydrogen). The molecular quantity requires 18·28 (approximately 18) grams of hydrogen, and the reaction evidently follows a course parallel to that occurring in the reduction of tetranitromethane, taking place as formulated on page 893.

Bromotrinitromethane.—This was prepared in the way described by Macbeth and Pratt (*loc. cit.*). 0·2502 Gram in 10 c.c. of alcohol required 157 c.c. of titanous chloride (16,166 c.c. = 2 grams of hydrogen). The molecular quantity therefore requires 17·86 (approximately 18) grams of hydrogen, and the reduction evidently takes place as formulated in the case of the chloro-compound.

Picryl Chloride.—This was prepared by Jackson and Gazzolo's method (*Amer. Chem. J.*, 1900, **23**, 384), and purified by repeated crystallisations. 0·9026 Gram was dissolved in 100 c.c. of alcohol and 15 c.c. of the solution required 92·2 c.c. of titanous chloride (16,600 c.c. = 2 grams of hydrogen). The molecular quantity therefore requires 20·3 (approximately 20) grams of hydrogen for complete reduction. The reaction therefore proceeds according to the equation:

$$C_6H_2Cl(NO_2)_3 + 10H_2 = C_6H_3(NH_2)_3 + HCl + 6H_2O.$$

Reduction of Dibromodinitromethane by Potassium Ferrocyanide.—Thirty grams of pure dibromodinitromethane (prepared from tribromoaniline) were added to a solution of 120 grams of potassium ferrocyanide in 500 c.c. of water [$CBr_2(NO_2)_2 : 2K_4Fe(CN)_6$ =

32 : 102]. The colour of the solution rapidly became darker on shaking and the potassium salt of monobromodinitromethane soon began to separate. After a few hours' shaking, the smell of the dibromodinitromethane had almost disappeared. The potassium salt was filtered off and washed twice with water, and then with alcohol. The yield of dry salt was 16 grams, or more than 60 per cent. of the theoretical, without taking into account the amount required to saturate the original 500 c.c. of water. No evolution of gas, nitrous fumes, or hydrocyanic acid was observed during the reaction. In addition to the potassium salt of monobromodinitromethane, the filtrate contained potassium bromide and potassium ferricyanide. No acidity is developed during the reduction, which proceeds according to the equation :

$$(NO_2)_2CBr_2 + 2K_4Fe(CN)_6 = (NO_2)_2CKBr + KBr + 2K_3Fe(CN)_6.$$

Bromination of Phenol by Bromotrinitromethane.—Twenty grams of bromotrinitromethane were added to a solution of 3 grams of phenol in 400 c.c. of water. About 15 c.c. of a cold, saturated, aqueous solution of hydrobromic acid (free from bromine) were added, and also about 40 c.c. of alcohol to increase the solubility of the bromonitroform in the solvent. The mixture was shaken in a machine for several hours, during which time the bromotrinitromethane disappeared and tribromophenol was precipitated. The solid was collected, dissolved in hot alcohol, and hot water (70°) added until precipitation of tribromophenol was just beginning; on cooling, tribromophenol crystallised out, the solvent retaining any unchanged bromonitroform. About 4 grams of recrystallised tribromophenol were obtained in this way. The filtrate from the crude tribromophenol was extracted several times with ether to remove the nitroform produced in the reaction. It may be isolated from the ethereal solution by careful evaporation, or obtained as the potassium salt by the addition of potassium ethoxide.

We desire to express our thanks to Professor Robinson, F.R.S., for the interest he has taken in the arguments put forward in the paper. One of us (T. H.) desires also to express thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has made participation in this research possible.

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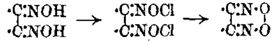
CIV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part II. Action of Hydrazine on Nitrogen–Halogen Compounds and on Bromomalonic Esters.*

By EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH.

ORGANIC compounds containing labile halogen atoms may, on the whole, be divided into two classes. In the first class we have such substances as acid chlorides, sulphonyl chlorides, and picryl chloride, which are characterised by the facility with which they undergo hydrolysis and by the ease with which replacement of the halogen atom by an amido-group occurs on treatment with ammonia; hydrazine hydrate also acts on such substances, the corresponding hydrazide being formed. In the second class may be placed compounds like the halogen-substituted, aliphatic polynitro-compounds, halogenated sulphonamides, and bromomalonic esters, which are not easily hydrolysed, but are readily reduced by hydriodic acid, the halogen atom being replaced by hydrogen. As there is no structure common to all the members of either class, the difference in the chemical behaviour of the halogen atom in the two types of compound cannot be explained merely on the grounds of the presence of a particular linking. For example, in picryl chloride, acetyl chloride, and benzenesulphonyl chloride, the chlorine atom is attached to a carbon atom, a carbonyl group, and a sulphur atom respectively; but in all these cases the halogen behaves chemically in the same way, the substances being readily converted into amides or hydrazides by the action of ammonia or hydrazine hydrate. On the other hand, the difference in structure of bromo-compounds such as bromonitroform, acetobromoamide, and bromomalonic ester is very marked, yet they all have in common the property of being readily reduced by hydriodic acid, and of oxidising hydrazine and other reagents. In a previous paper (Henderson and Macbeth, this vol., p. 892) it has been pointed out that if the polarities of the constituent atoms of the molecule are considered, the chemical behaviour of the two types of labile halogen may readily be accounted for; the chlorine atom in the compounds referred to above is of a strongly electro-negative nature and therefore it is not surprising that picryl chloride displays the principal reactions of an acid chloride. On the other hand, the bromine atom in all the compounds considered is of a strongly electro-positive nature and therefore readily reacts with reducing agents. Representative types of both classes have been given (*loc. cit.*).

It may, however, be contended that the labile nature of the halogen may be accounted for by structural considerations. In the alkyl haloids, where the halogen is attached to a carbon atom and there is no possibility of migration, the substances are extraordinarily stable in the presence of hydrolytic and reducing agents when compared with compounds of the type referred to above. In the case of the bromo-compounds mentioned, although the bromine is supposedly attached to carbon, there is a possibility of its migration to an oxygen atom producing the halogen analogues of the sodium derivatives of nitroform and malonic ester. It has been suggested (Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1775) that the labile nature of the halogen atom in bromonitromalonic ester and the nitroparaffin derivatives is due to this cause. There are strong grounds for believing that a halogen atom attached to oxygen would be very reactive, although the view rests more on inference than on direct experimental proof. Mohlau (*Ber.*, 1886, **19**, 280; 1887, **20**, 1504), investigating the action of sodium hypochlorite on acetoxime, believed that he had isolated the chloro-oxime, $(CH_3)_2C{:}NOCl$, in which the chlorine was very reactive. Ponzio (*Atti R. Accad. Sci. Torino*, 1906, **41**, 415, 862) showed that the above record was incorrect, and that the chlorine migrates to the carbon atom, with the ultimate formation of α-chloro-α-nitropropane, $(CH_3)_2CCl{\cdot}NO_2$. He further found that the general effect of hypochlorites on aromatic oximes and dioximes was the production of peroxides. In the light of the behaviour of acetoxime, this reaction may be interpreted as a chlorination process, an intermediate compound being formed in which there is a halogen–oxygen linking, but in which the halogen atom is so labile that the compound decomposes almost immediately even in the cold :



Along with the peroxide a small amount of the azoxime is produced, and its formation may also be represented as due to a process of chlorination.

It seems reasonable to assume, however, that although there are grounds for believing that the halogen atom would prove very reactive in an oxygen–halogen linking, this structure does not occur in the nitroparaffins or in the malonic series. It is hoped later to produce direct evidence against this view. At present we are of the opinion that the chemical differences observed in the two classes of reactive compounds are best accounted for by taking into consideration the alternate effect due to the negative polarities of the

oxygen atoms, which results in strongly electro-positive or electro-negative halogen atoms.

It has been shown that substances containing an electro-positive halogen atom, in addition to being reduced by hydriodic acid, are also reduced by acid solutions of titanous chloride (Henderson and Macbeth, *loc. cit.*). Further, since reduction readily takes place, it is not to be expected that ammonia and hydrazine will act on such substances to give substitution products such as are obtained with acid chlorides; but oxidation of the bases will occur instead. The action of hydrazine has already been studied in the case of some aliphatic nitro-compounds (Macbeth and Pratt, T., 1921, **119**, 1356) and it was found that reduction of the halogen compound took place, nitrogen being quantitatively evolved from the hydrazine. As a result of further work it would appear that this reagent is of value, not only in demonstrating the labile nature of the halogen atom in organic compounds, but also in furnishing a ready and trustworthy means of estimating the halogen content of such substances. In this communication the reaction with nitrogen–halogen compounds, such as *N*-chloroacetanilide, acetobromoamide, and sulphondichloroamides is described; and the effect on a series of bromomalonic esters is also recorded.

The estimations were carried out, as in previous work (*loc. cit.*), with a Van Slyke nitrometer. Slight modifications are necessary in the case of the different substances, and these are referred to in the experimental part. The nitrogen–halogen compounds all react very vigorously with hydrazine hydrate, and the nitrogen is evolved almost immediately. The reaction is quantitative, as the nitrogen is evolved in accordance with the following general equations:

$$R\cdot SO_2\cdot NCl_2 + NH_2\cdot NH_2 = R\cdot SO_2\cdot NH_2 + N_2 + 2HCl \quad . \quad . \quad (1)$$

$$2R\cdot SO_2K{:}NCl + NH_2\cdot NH_2 = 2R\cdot SO_2K{:}NH + N_2 + 2HCl \quad . \quad (2)$$

N-Chloroacetanilide and acetobromoamide also react vigorously, the reactions proceeding quantitatively as follow:

$$2C_6H_5\cdot NCl\cdot CO\cdot CH_3 + NH_2\cdot NH_2 = 2C_6H_5\cdot NH\cdot CO\cdot CH_3 + N_2 + 2HCl.$$

$$2CH_3\cdot CO\cdot NHBr + NH_2\cdot NH_2 = 2CH_3\cdot CO\cdot NH_2 + N_2 + 2HBr.$$

In all the above cases the reaction proceeds, as far as can be judged, at the same rate. It may therefore be concluded that the reactivity of the halogen atom is of much the same order in all the nitrogen haloids examined. The reaction proceeds somewhat more quickly than in the case of substituted nitroform, and the halogen atom in this may be regarded as a little more stable.

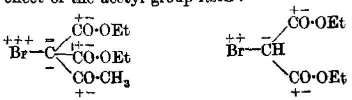
Monobromo- and dibromo-malonic esters also react quickly with hydrazine, but the liberation of the nitrogen extends over one

minute. The substituted esters also react, but the time required for complete reduction is longer and increases as substitution proceeds. Thus bromomethylmalonic (bromo*iso*succinic) ester takes from three to five minutes to react, and there is a remarkable decrease in the rate of reaction in the case of the higher members. Bromoethyl-, bromo*iso*propyl-, bromobutyl-, and bromo*iso*butyl-malonic esters all liberate the nitrogen slowly from hydrazine, and two to three hours are required to complete the reaction. In these cases, the results obtained are slightly low, and this may be due to incomplete reaction. In this connexion, however, it may be pointed out that Fischer (*Ber.*, 1906, **39**, 351) showed that the *iso*butylmalonic ester prepared in the course of his work was never obtained quite pure, and always contained a small amount of a product which was hydrolysed by alkali with difficulty. He suggested that this was probably the di*iso*butylmalonic ester. If a small amount of the dialkylmalonic ester were present in the higher esters employed in our brominations, it would be present also in the brominated ester, as it is not easily removed by fractionation. Its presence would account for the slightly low results obtained, and the reactions, although slow, might be regarded as taking place quantitatively. The following equations express the reaction :

$$Br_2C(CO_2Et)_2 + NH_2{\cdot}NH_2 = CH_2(CO_2Et)_2 + N_2 + 2HBr \quad . \quad (3)$$

$$2CRBr(CO_2Et)_2 + NH_2{\cdot}NH_2 = 2CHR(CO_2Et)_2 + N_2 + 2HBr \quad (4)$$

The decrease in the rate of reaction observed in the case of the more highly substituted esters may be accounted for by the steric effect of the substituents; the great decrease on passing from the methyl to the ethyl derivative is noteworthy. The results obtained are quite comparable, as the conditions of the different experiments were the same and the solutions of the bromo-esters employed were of corresponding strengths. In connexion with the steric effect, the results obtained with acetylbromomalonic ester may be referred to. The time of reaction for this compound was intermediate between that observed in the case of bromomalonic ester and its methyl derivative, and the steric effect in this case is evidently modified by the nature of the acetyl group. The oxygen in its carbonyl group being in the α-position to the carbon to which the bromine is attached makes the halogen more electro-positive; and this increase in the positiveness of the bromine atom largely counterbalances the steric effect of the acetyl group itself :



The labile halogen compounds may be placed in different grades according to the results obtained. The nitrogen-haloids show the greatest lability, and close to these come the nitro-compounds which contain two or more nitro-groups attached to the same carbon. In the next grade may be placed the unsubstituted bromomalonic esters, the lability of the halogen decreasing when substitution occurs and as more complex substituents are introduced. In the case of the halogen compounds which contain the halogen attached to a carbon atom, certain conditions must be present in the molecule before lability becomes marked. Thus two carbonyl groups in the α-positions are required before the halogen is sufficiently labile to be reduced by hydrazine hydrate in the cold. These conditions are present in the bromomalonic esters and bromoacetoacetic ester, and these are reactive; but no nitrogen is liberated from hydrazine at the ordinary temperature by such substances as chloroacetone, ethyl chloroformate, bromoacetic acid, chloroacetic acid, trichloroacetic acid, and other compounds of a similar type which do not contain the minimum two carbonyls required. Similar observations are noted in the case of the nitro-compounds, and here it would appear that at least two nitro-groups attached to the same carbon are necessary to endow the halogen with a positiveness sufficient to make it labile in the presence of hydrazine.

This observation is sufficiently illustrated by reference to the behaviour of monobromonitromethane and dibromodinitromethane. The latter reacts with hydrazine in the cold and one of the halogen atoms is removed (Macbeth and Pratt, *loc. cit.*); both bromine atoms are removed by treatment with arsenious oxide in the presence of alkali (Duden, *Ber.*, 1893, **26**, 3004). The halogen atom in monobromonitromethane, on the contrary, withstands the action of such reducing agents.

It would also appear that the polarity present in the molecule which is sufficient to endow a halogen atom with reactivity is not sufficient to render a nitro-group labile. Thus the two nitro-groups in dibromodinitromethane make the halogen reactive towards hydrazine and other reducing agents; but the third nitro-group in nitroform is not affected by such treatment. In the same way, the bromine atom in the bromomalonic esters is reactive, but the polarity of the two carbethoxy-groups is not sufficient to endow the nitro-group in nitromalonic ester with similar chemical properties. This resistance to reduction cannot be connected with *aci*-salt formation of the nitro-group in the presence of alkaline reagents, for the group is not removed on treatment with acid reducing agents, such as titanous chloride.

The action of reducing agents on halogen compounds is being

further studied, and it is hoped to communicate later the results obtained with hydrazine and a series of bromomalonamides, and the action of ammonia and titanous salts on a number of representative substances.

Experimental.

The estimations were carried out in the usual way with a Van Slyke nitrometer. Hydrazine hydrate (50 per cent. solution) was used in all cases, and 1 c.c. furnished a sufficient excess for the quantities of the halogen compounds employed in the experiments.

Benzenesulphondichloroamide was prepared by Chattaway's method (T., 1905, **87**, 145). 0·226 Gram of the finely powdered sulphondichloroamide was washed into the nitrometer with as small a quantity of alcohol as possible. 23·4 C.c. of nitrogen were liberated at 13° and 760 mm. The molecular quantity (226 grams) of the sulphondichloroamide liberates 28·06 grams of nitrogon, so the reaction is represented by equation (1), where R = Ph.

Potassium benzenesulphonchloroamide was prepared by Chattaway's method (*loc. cit.*) and dried on the water-bath. 0·459 Gram, washed into the nitrometer with a little water, liberated 23·5 c.c. N_2 at 14° and 756 mm. The bimolecular quantity (459 grams) liberates 27·93 grams N_2, so the reaction follows the course of equation (2), where R = Ph.

Potassium 2-nitrotoluene-p-sulphonchloroamide was prepared by Chattaway's method (*loc. cit.*). 0·5380 Gram liberated 20·7 c.c. N_2 at 13° and 733 mm. The bimolecular quantity liberates 27·28 grams N_2; Cl present as NCl = 11·3 (theoretical, 11·59 per cent.). An independent method gave 11·35 per cent. (The sample was partly dehydrated.)

2-Nitrotoluene-p-sulphondichloroamide.—An impure sample was examined, and 0·285 gram liberated 17·2 c.c. N_2 at 13° and 734 mm. The molecular quantity liberates 19·92 grams N_2, so the purity of the substance is 71·08 per cent. An independent method gave 71 per cent.

Chloroamine T.—A commercial sample was dried on the water-bath and examined. 0·455 Gram liberated 22·4 c.c. N_2 at 16° and 760 mm. The bimolecular quantity liberates 26·57 grams N_2, or the sample contains 94·88 per cent. of *p*-toluenesulphonchloroamide.

Dichloroamine T.—0·240 Gram of a commercial sample liberated 23·3 c.c. N_2 at 16° and 760 mm. The sample therefore contains 98·68 per cent. of *p*-toluenesulphondichloroamide.

Benzenesulphondibromoamide.—An impure sample was examined; 0·317 gram gave 13·7 c.c. N_2 at 13° and 732 mm. The percentage purity was therefore 56·5. An independent method gave 56·2 per cent.

N-Chloroacetanilide was prepared by Chattaway and Orton's method (T., 1899, **75**, 1046). 0·3390 Gram, washed into the nitrometer with alcohol (water must not be used as it causes the separation of acetanilide formed in the reaction, which carries down the chloro-compound and gives too low a result), liberated 23·3 c.c. N_2 at 13° and 720 mm.; Cl as NCl = 19·65 per cent. An independent method gave the value 19·79 per cent. The purity is therefore about 94 per cent.

Acetobromoamide was prepared by Behrend and Schreiber's method (*Annalen*, 1901, **318**, 373). 0·276 Gram liberated 11·2 c.c. N_2 at 13° and 739 mm.; Br as NBr = 26·84 per cent. An independent method gave 26·88 per cent. The percentage purity is therefore about 46·35.

Ethyl bromomalonate was prepared by Knoevenagel's method (*Ber.*, 1888, **21**, 1355). 2·390 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 23·7 c.c. N_2 at 14° and 748 mm. *The nitrogen was completely evolved in less than one* minute. The bimolecular quantity therefore liberates 27·88 grams N_2, and equation (4) represents the reaction (R = H).

Ethyl dibromomalonate was prepared by Conrad and Brückner's method (*Ber.*, 1891, **24**, 3001). 1·590 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 24·0 c.c. N_2 at 10° and 737 mm. The evolution was complete in a little more than a minute. The molecular quantity therefore liberates 28·2 grams N_2, and the reaction is expressed by equation (3).

Propyl Bromomalonate.—Propyl malonate was brominated in the usual way, and after washing with a dilute solution of sodium hydroxide and with water, the bromo-ester was dried over calcium chloride and fractionated; b. p. 135°/12 mm. 1·068 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 25 c.c. N_2 at 17° and 726 mm. The nitrogen was completely evolved in about a minute, so there is no difference in the reactivities of the ethyl and propyl esters. The reaction is quantitative and proceeds in accordance with the typical equation (4).

Ethyl bromoisosuccinate was prepared by Wheeler and Johnson's method (*J. Amer. Chem. Soc.*, 1902, **24**, 686). 2·530 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 23·8 c.c. N_2 at 16° and 756 mm. The nitrogen was evolved slowly, but steadily, the reaction being complete in about six minutes. The bimolecular quantity liberates 28·1 grams N_2, so the reaction proceeds quantitatively.

Ethyl bromoethylmalonate was prepared by Ruhemann's method (*Ber.*, 1893, **26**, 2357). 2·670 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 22·8 c.c. N_2 at 15° and

mm. The nitrogen was slowly evolved, the reaction extending r three hours. The bimolecular quantity liberates 27·0 grams N_2, the result is about 4 per cent. too low. This may be due to omplete reaction, or to the presence of some diethylmalonic er in the bromo-compound (see Fischer, *loc. cit.*).

Ethyl bromoisopropylmalonate, prepared by Conrad and Bischoff's thod (*Annalen*, 1880, **204**, 144), and *bromoisobutylmalonate* ıthzeit, *Annalen*, 1881, **209**, 236; Fischer and Schmitz, *Ber.*,)6, **39**, 351) were also examined. In these cases the nitrogen s slowly liberated, and the reaction extended over three to four urs. The results obtained were about 2 per cent. too low.

Ethyl Acetylbromomalonate.—This was prepared by the slow dition of bromine to acetylmalonic ester, and purified by washing th dilute sodium hydroxide to remove hydrobromic acid and cess of bromine. After drying over calcium chloride, it boiled 130°/10 mm. It reacted quickly with hydrazine, the nitrogen ing completely evolved in less than two minutes. 0·594 Gram ıve 25·4 c.c. N_2 at 16° and 757 mm.; Br = 28·8 (calc., Br = 3·47 per cent.).

Ethyl nitromalonate was prepared by Wahl's method (*Compt. nd.*, 1901, **132**, 1052). It did not liberate nitrogen when acted n by hydrazine hydrate.

Ethyl bromonitromalonate was prepared by Willstätter and Hotenroth's method (*Ber.*, 1904, **37**, 1780). 2·84 Grams were dissolved n 25 c.c. of alcohol, and 5 c.c. of this solution liberated 24·4 c.c. N_2 at 13° and 733 mm. The bimolecular quantity therefore iberates 28·19 grams N_2, so the bromine is quantitatively removed. The reaction proceeds more quickly than with bromomalonic ester, the nitro-group reinforcing the effect of the two carbonyl groups.

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CV.—*Derivatives of 2-Hydroxybenzanthrone. Part I.*

By GEOFFREY GORDON BRADSHAW and ARTHUR GEORGE PERKIN.

IT has been shown by one of us (A. G. Perkin, Brit. Pat. No. 151707, 1920) that the product obtained when anthraquinone is heated under pressure with dextrose and alkali solution gives an almost quantitative yield of anthranol on treatment with acid. It seemed likely that this process might be generally applicable for the conversion

of hydroxyanthraquinones into their anthranols, or, indeed, a more drastic reduction might occur with the production of dianthryl and anthracene derivatives (Perkin and Whattam, this vol., p. 289). As the result of experiments with 2-hydroxyanthraquinone, dextrose, and alkali, although there is reason to presume that the initial product is 3-hydroxyanthranol, the reaction proceeds further with the formation of substances of a somewhat unexpected character. These are described below.

EXPERIMENTAL.

Crude 2-hydroxyanthraquinone (5 grams), prepared from commercial 2-aminoanthraquinone, was treated in the form of a 32 per cent. paste with a solution of sodium hydroxide (6·3 grams) and dextrose (5 grams) in water (23 c.c.), and this mixture was heated in an autoclave for eight hours at 170—180°. The product dissolved in water, giving a brown liquid possessing an intense green fluorescence, and from this, by acidification in the cold, a semi-resinous precipitate (*A*) separated. This was collected, dried on tile, well ground, and in the earlier experiments stirred up with a little pyridine, when the solution, on keeping, deposited a small amount of yellow powder, the alkali salts of which gave fluorescent solutions. Some loss of substance had, however, occurred, and as it was subsequently ascertained that this yellow compound possessed the properties of an acid, the following method was adopted for its isolation.*

The precipitate *A*, suspended in much water, was dissolved by addition of sodium hydroxide and carbonic acid gas passed through the liquid. The resinous precipitate (*A*) was removed, again treated twice in the same manner, and the combined liquids acidified with hydrochloric acid. A yellowish-brown deposit separated which became viscid on keeping, and this was collected and allowed to dry at the ordinary temperature (yield 2·4 grams). The finely ground product, stirred into about its own volume of acetone, gave at first an almost clear solution, but this rapidly commenced to deposit yellow crystals and became semi-solid on keeping. These were collected, well washed with acetone, and dried (*C*). The yield was 0·8 gram. For purification, crystallisation from alcohol may be employed, but a more satisfactory result is obtained by the use of boiling acetic anhydride. The partly concentrated solution deposited crystals on cooling,† which were again treated in a similar manner, employing animal charcoal, and the product was

* This may also be effected by extracting the crude material with boiling sodium acetate solution and acidifying the extract.

† The acetic anhydride mother-liquor is referred to later as (*B*).

ally crystallised from nitrobenzene (Found : C = 79·2; H = 3·16. $_{18}H_8O_3$ requires C = 79·41; H = 2·94 per cent.).

This new substance consists of orange-yellow needles melting at 5—317°, and is sparingly soluble in the usual solvents. In cold kaline solutions, it is insoluble, but on boiling it gradually dissolves, giving orange-yellow liquids which possess an intense green fluorescence. The solution in sulphuric acid is also fluorescent. Experiment showed that an acetyl group was not present, and as the original material had the property of an acid, it appeared likely that lactone formation had occurred as a result of the action of the acetic anhydride. To test the validity of this supposition, the substance $C_{18}H_8O_3$ (0·5 gram), suspended in 20 c.c. of boiling alcohol, was treated with 1 c.c. of strong ammonia, causing the separation of a semi-solid mass of minute, yellow needles consisting evidently of an ammonium salt. Addition of a little water gave a clear solution, from which, on acidification at the boiling point, fine needles separated (Found : C = 74·75; H = 3·99. $C_{18}H_{10}O_4$ requires C = 74·5; H = 3·45 per cent.).

This compound, now readily soluble in alkaline liquids, is evidently the free acid; it closely resembles the lactone in appearance. It can again be readily transformed into the latter by dehydrating agents, and this change evidently occurs on heating, as it sinters at about 275° and is completely fused only at 315°.

The lactone, $C_{18}H_8O_3$ (0·5 gram), digested with 3 c.c. of diethylamine at the boiling point, quickly deposited crystals, and on adding a little dilute alcohol and cautiously neutralising the clear liquid with hydrochloric acid, large, orange-yellow leaflets separated. These are readily soluble in alcohol (Found : C = 72·65; H = 5·9; N = 3·63. $C_{18}H_{10}O_4,C_4H_{10}N$ requires C = 72·5; H = 6·04; N = 3·84 per cent.).

The formation of this compound, which is evidently a *diethylamine* salt, proceeds almost quantitatively, since the yield was 129·5 per cent., whereas theory requires 133 per cent.

The acid $C_{18}H_8O_4$ gradually dissolves in boiling aniline. After digestion for forty minutes, the liquid on cooling deposited crystals which were collected, washed with alcohol, and recrystallised from this solvent (Found : C = 79·3; H = 4·4; N = 3·94. $C_{24}H_{15}O_3N$ requires C = 78·90; H = 4·11; N = 3·84 per cent.).

This *anilide* consists of fine, flat, yellow needles which melt at 274—276° and dissolve in alkaline liquids with formation of green, fluorescent solutions. To obtain further evidence of the presence of the hydroxyl group in the acid $C_{18}H_8O_4$, 0·5 gram, suspended in 6 c.c. of cold pyridine, was treated with 3 c.c. of acetic anhydride, these conditions being employed so as to avoid lactone

formation. The orange-yellow needles did not dissolve, but gradually became pale yellow, and after keeping over-night the product was collected, washed with alcohol, and recrystallised from acetic acid [Found : C = 72·95 ; H = 4·26. $C_{18}H_9O_4(C_2H_3O)$ requires C = 72·3 ; H = 3·67 per cent.].

On heating, this *acetyl* derivative appears to suffer gradual decomposition, and does not possess a definite melting point. By hydrolysis in boiling acetic acid solution with fuming hydrochloric acid, the yield of regenerated acid was 85·09 per cent., whereas theory requires $C_{18}H_{10}O_4$ = 87·35 per cent. These somewhat low figures were found to be due to a conversion during the hydrolysis of a small portion of the acid into its lactone, but in any case the result is sufficiently accurate to indicate the presence of one acetyl group.

Methylation.—The lactone, suspended in methyl alcohol, was repeatedly treated with equivalent amounts of methyl sulphate and methyl-alcoholic potassium hydroxide, the mixture being boiled after each addition. The methylation process occurred only slowly, and very large quantities of these reagents were necessary. The mixture was partly evaporated, hot water cautiously added, and the crystalline precipitate which separated washed with dilute sodium hydroxide solution and recrystallised from methyl alcohol [Found : C = 75·66 ; H = 4·46 ; CH_3 = 19·29. $C_{18}H_8O_2(O{\cdot}CH_3)_2$ requires C = 75·50 ; H = 4·40 ; CH_3 = 19·49 per cent.].

This *dimethyl* compound consists of long, yellow needles melting at 185—186° and is somewhat readily soluble in boiling alcohol. Sulphuric acid dissolves it, to form an orange solution possessing a green fluorescence, and nitric acid behaves similarly. A hot solution in glacial acetic acid, when treated with sulphuric acid, deposited on cooling orange needles which became red on drying. Owing to the ready solubility of this compound, evidently an oxonium sulphate, in acetic acid, its analysis was not attempted. When a solution containing 0·5 gram of the dimethyl compound in 8 c.c. of boiling acetic acid was treated with 0·5 gram of anhydrous ferric chloride in 8 c.c. of acetic acid, a red coloration developed and, on cooling, crystals of the *ferrichloride oxonium salt* separated. These were washed with acetic acid, and, when dry, formed a scarlet mass of fine needles. Treatment with water regenerated the methyl ether, and this method was employed for analysis [Found : $C_{20}H_{14}O_4$ = 76·13 ; Cl = 16·79. $(C_{20}H_{14}O_4)_2,HFeCl_4$ requires $C_{20}H_{14}O_4$ = 76·19 ; Cl = 16·99 per cent.].

The *stannichloride* prepared from 0·5 gram of the substance in 20 c.c. of acetic acid and 0·5 gram of anhydrous stannic chloride in 10 c.c. of acetic acid separated as hair-like, scarlet needles

[Found : $C_{20}H_{14}O_4$ = 68·52; 68·54. $(C_{20}H_{14}O_4)_2,SnCl_4,HCl$ requires $C_{20}H_{14}O_4$ = 68·14 per cent.].

The *platinichloride* was obtained as bright red, prismatic needles [Found : Pt = 14·72; 14·26. $(C_{20}H_{14}O_4)_3,H_2PtCl_6$ requires Pt = 14·31 per cent.].

As the product of the methylation, $C_{20}H_{14}O_4$, evidently contains both a phenolic and a carbomethoxy-group, experiments were now carried out with the object of obtaining the methoxycarboxylic acid.

The dimethyl compound (0·4 gram) was digested with 20 c.c. of 10 per cent. alcoholic potassium hydroxide on the water-bath, when fine, orange needles of a potassium salt were quickly deposited. After heating for an hour, the addition of hot water yielded a clear fluorescent solution, and from this, by acidifying, a crystalline precipitate separated. This, when recrystallised from alcohol, sintered at about 275°, finally melted at 314—316°, and had the properties of the hydroxy-acid, $C_{18}H_{10}O_4$. By this treatment, therefore, not only the carboxylic ester, but also the methoxy-group, had suffered hydrolysis.

In a second experiment, a solution of the dimethyl compound, $C_{20}H_{14}O_4$, in 10 parts of cold sulphuric acid was allowed to stand for three hours. The product was poured into water, the mixture boiled, and the crystalline precipitate collected and recrystallised from alcohol. Thus obtained, it dissolved completely in dilute ammonia, and when heated commenced to sinter at 270° and melted at 277—279° [Found: CH_3 = 4·61. $C_{18}H_9O_3(O{\cdot}CH_3)$ requires CH_3 = 4·90 per cent.].

This product, although it consisted mainly of the methoxycarboxylic acid, was evidently not quite pure, and even under these conditions some demethylation of the methoxy-group had taken place. Thus it was ascertained that by a treatment with cold sulphuric acid extending over several days, complete demethylation occurred, the product by digestion with acetic anhydride being then entirely converted into the lactone $C_{18}H_8O_3$.

Attempts to remove the carboxyl group from the acid $C_{18}H_{10}O_4$ by fusion with potassium hydroxide at 230—240° for one hour failed, most of the original substance being recovered unchanged. At 250—260°, decomposition slowly occurred, and a dark brown amorphous product, soluble in alkali without fluorescence, was produced.

Distillation with Zinc Dust.—The lactone, $C_{18}H_8O_3$ (1 gram), was distilled with zinc dust in a current of hydrogen according to the well-known method of Gattermann. The red, crystalline deposit which had collected in the cool portion of the tube was removed, extracted with boiling alcohol, the solution decolorised with animal

charcoal, and evaporated to a small bulk. Pale brownish-yellow needles, melting at 78°, separated, and these dissolved in sulphuric acid, forming a red solution which possessed a brown fluorescence. As it was suspected that this hydrocarbon was impure benzanthrene, both the 2-hydroxybenzanthrone prepared from 2-hydroxyanthraquinone and benzanthrone itself were respectively distilled with zinc dust. The product in each case after purification consisted of greenish-yellow leaflets melting at 80°, and these, admixed with the hydrocarbon derived from the lactone, melted at 79—80°. According to Bally and Scholl (*Ber.*, 1911, **44**, 1667), benzanthrene readily oxidises in presence of air. It melts at 84°, but to obtain the pure substance special precautions are necessary in order to exclude air during its purification. Such a treatment in this case was not adopted and the product was now digested in acetic acid solution with a little ferric chloride. On cautious dilution with hot water, pale yellow needles separated which melted at 165° and proved, as the result of a mixed melting-point determination, to be identical with benzanthrone. It accordingly seems certain that the acid $C_{18}H_{10}O_4$, which so readily yields the lactone $C_{18}H_8O_3$, consists of a hydroxybenzanthronecarboxylic acid.

Oxidation of the Dimethyl Ether.—To a solution of the substance (1 gram) in 20 c.c. of acetic acid, 5·5 c.c. of a solution of 1 part of chromic acid in 2 parts of 50 per cent. acetic acid were added drop by drop. A vigorous reaction occurred, and on keeping, the liquid deposited pale yellow plates. By recrystallisation from acetic acid after decolorising with animal charcoal, it was obtained in an almost colourless condition and melted at 267—268°. The product was insoluble in alkaline solutions, and on exposure to light gradually acquired a reddish-brown tint [Found: C = 66·41; H = 3·96; CH_3 = 8·86. $C_{16}H_8O_4(O{\cdot}CH_3)_2$ requires C = 66·66; H = 3·70; CH_3 = 9·26 per cent.].

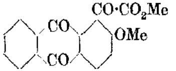
As it seemed probable that this substance was the ester of a carboxylic acid, it was digested for a short time with dilute alcoholic potassium hydroxide at the boiling point. Water was added, the alcohol boiled off, and the clear liquid acidified. Almost colourless needles separated melting at 275°.

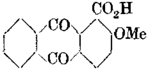
In a second experiment, a solution of the substance $C_{18}H_{14}O_6$ in sulphuric acid was heated on the water-bath for a few minutes, during which time the orange-red colour of the liquid quickly changed to green and sulphurous acid was evolved. The addition of water caused a dull violet precipitate to separate and this was collected, dissolved in dilute ammonia, and the reddish-brown solution decolorised at the boiling point with animal charcoal. On acidification, greyish-white needles were deposited, which melted at 275°

[*Found* : C = 67·9; H = 3·69; CH_3 = 5·33. $C_{14}H_6O_2(O{\cdot}CH_3){\cdot}CO_2H$ requires C = 68·08; H = 3·54; CH_3 = 5·32 per cent.].

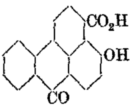
It has been shown (Perkin, T., 1920, **117**, 700; Perkin and Spencer, this vol., p. 478) that the methyl ether of the 2-hydroxybenzanthrone derived from 2-hydroxyanthraquinone gives by oxidation a methoxyanthraquinonecarboxylic acid melting at 276°. As it appeared probable that the acid just described was identical with the latter, a mixed melting-point determination was carried out, which proved this to be the case.

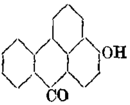
It seems evident, therefore, that the first product, $C_{18}H_{14}O_6$, of the oxidation of the methylated acid, $C_{20}H_{14}O_4$, is methyl 2-methoxyanthraquinone-1-glyoxylate (I), and that this passes by hydrolysis and elimination of carbon dioxide into 2-methoxyanthraquinone-1-carboxylic acid (II).

(I.) 

 (II.)

The *fact that the first-named ester contains the two methyl-groups* present in the original compound before oxidation affords proof of the positions of the methoxy- and glyoxylic acid ester-group, the former of which is naturally in the 2-position on account of its derivation from 2-hydroxyanthraquinone. There is a very close resemblance in properties between the acid $C_{18}H_{10}O_4$ derived from 2-hydroxyanthraquinone by means of dextrose and alkali and the 2-hydroxybenzanthrone which is also prepared from the latter compound by means of glycerol and sulphuric acid. Thus both give with dilute alkali intensely fluorescent solutions, both are extremely stable towards fused alkali, and again from their methylation products well-characterised, scarlet oxonium salts can be obtained. It therefore seems certain that the former is a carboxylic acid of the latter, and again the readiness with which this hydroxy-acid undergoes lactone formation indicates that its hydroxy- and carboxyl-groups are in the peri-position to one another. The constitution of the acid $C_{18}H_{10}O_4$ is thus considered to be represented by III and this affords additional evidence (Perkin and Spencer, *loc. cit.*) that the hydroxybenzanthrone above referred to possesses the hydroxyl group in the 2-position (IV).

(III.) 

 (IV.)

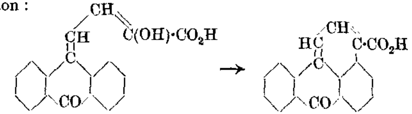
The production of hydroxybenzanthronecarboxylic acid from 2-hydroxyanthraquinone by treatment with alkali and dextrose rendered it likely that other sugars and the allied alcohols might be also efficient for this purpose. A mixture of lævulose (12 grams), 2-hydroxyanthraquinone (12 grams), sodium hydroxide (15 grams), and water (90 c.c.) was heated at 200° for seven hours, and the product worked up as previously described. The result was practically identical with that given in the case of dextrose, there being obtained after the acetone treatment 1·9 grams of crude carboxylic acid, which yielded 0·8 gram of the pure lactone. In a second experiment the lævulose was replaced by 12 grams of mannitol, with a similar result, the yield of crude carboxylic acid being 1·4 grams and of pure lactone 0·45 gram.

More specially interesting was the formation of the hydroxybenzanthronecarboxylic acid from 2-hydroxyanthraquinone (12 grams), sodium hydroxide (15 grams), and erythritol (12 grams). Though owing to its expensive nature erythritol could not be employed in large amount, it proved to be far the most effective reagent for this purpose. Thus the product isolated by means of carbon dioxide (3·2 grams), being free from viscid impurity, required no treatment with acetone, and by one treatment with acetic anhydride gave the pure lactone melting at 317—319°. Again, it was ascertained that glycerol is serviceable for this purpose; the crude product thus obtained is purer than that given by dextrose. This, after recrystallisation from acetic anhydride, melted at 317—318° (Found: C = 79·50; H = 2·94 per cent.).

Finally, it was noted that if in these experiments 3-hydroxyanthranol is employed in the place of the 2-hydroxyanthraquinone, no difference is to be observed in the resulting products. There can indeed be little doubt that when 2-hydroxyanthraquinone is submitted to the action of dextrose and alkali its anthranol represents the first stage of the reaction.

The action of alkaline oxidising agents on sugars, which is profound even at the ordinary temperature (Nef, *loc. cit.*), must be even more complex at the high temperature here employed, so that the theoretical reasons which can be suggested to account for the benzanthrone formation in this remarkable manner must necessarily be, at least at present, of a speculative character. In attempting to explain the mechanism of this reaction, the case of erythritol is the simplest, because this substance contains just the necessary four carbon atoms for the transformation. This, by the oxidising action of the 2-hydroxyanthraquinone, it is assumed, may pass first into erythrose and then into the apparently unknown β-aldehydo-αβ-dihydroxypropionic acid, $CHO\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$.

This by loss of water will yield the acid $CHO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$,* which, reacting in its tautomeric modification, $CHO{\cdot}CH{:}C(OH){\cdot}CO_2H$, on the hydroxyanthranol, is probably responsible for the benzanthrone formation :



In extending such a theory to this benzanthrone synthesis by means of dextrose, mannitol, and lævulose, it appears not impossible that the trihydroxybutyric acids which have been found by Nef (*Annalen*, 1907, **357**, 214; 1910, **376**, 1; 1914, **403**, 204) among the products arising from the alkaline oxidation of dextrose, and which with little doubt will result in a similar manner from mannitol and lævulose, may be serviceable for this reaction. Thus from these by the oxidising action of the 2-hydroxyanthraquinone according to the scheme indicated above, the acid $CHO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$ can also be assumed to originate. On the other hand, a possibility suggests itself of the union of the dextrose with the anthranol by means of its aldehydic group in the first instance, although, as anthranol formation does not occur in these circumstances except at elevated temperatures, such a reaction is unlikely.

That the effect of glycerol, containing as it does only three of the necessary four carbon atoms, is here identical with that of dextrose, is difficult to understand. By the interaction of its oxidation products a condensation will presumably occur, the resulting compound being subsequently degraded, at least in part, with formation of the necessary four-carbon complex.

Other Products of the Reaction.

In addition to the 2-hydroxybenzanthronecarboxylic acid obtained from 2-hydroxyanthraquinone by the dextrose–alkali process, three other crystalline compounds have been isolated in small amount both from the acetic anhydride mother-liquor (*B*) and the resinous precipitate (*A*).

In the former case, (*B*) was diluted with much water, the precipitate collected, dried at the ordinary temperature, and treated with a little acetone. The residue, after recrystallisation from acetone, was digested with boiling benzene, by which treatment a yellow, crystalline substance (*D*), soluble in sulphuric acid with a crimson coloration and which is referred to later, remained undissolved.

* This acid is apparently also unknown, but its chloro-derivative, β-chloro-α-hydroxy-β-formylacrylic acid, $CHO{\cdot}CCl{:}C(OH){\cdot}CO_2H$, has been prepared by Hill and Palmer (*J. Amer. Chem. Soc.*, 1887, **9**, 160).

The filtrate on evaporation deposited orange leaflets, and to remove a trace of *D* still present these were extracted with acetone. The crystals obtained by evaporating the extract were again recrystallised from acetone * [Found : C = 77·4 ; H = 3·9. $C_{28}H_{14}O_4(C_2H_3O)_2$ requires C = 77·1 ; H = 3·66 per cent.].

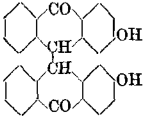
This *acetyl* compound, when heated, partly fused between 160° and 170°, on further heating solidified, and finally melted at 276°. Sulphuric acid dissolves it with a fine violet coloration, whereas its *solution in benzene possesses an intense green fluorescence.* By hydrolysis with fuming hydrochloric acid in presence of acetic acid, 83·2 per cent. of the free hydroxy-compound was isolated in the form of an orange-red powder, whereas the above formula requires $C_{28}H_{16}O_4$ = 83·2 per cent. The product, recrystallised from a large volume of acetone, was obtained as orange-red needles (Found: C = 80·79; H = 3·76. $C_{28}H_{16}O_4$ requires C = 80·76; H = 3·84 per cent.).

Heated above 300°, it apparently suffered decomposition, and had not completely fused at 350°. Sulphuric acid dissolves it with a bluish-violet coloration, and dilute alkalis with a red tint similar to that given by 2-hydroxyanthraquinone. This compound can be readily methylated by diazomethane in the presence of pure acetone. The orange product, by recrystallisation from dilute acetic acid, was obtained as needles melting at 276° [Found : C = 80·95; H = 4·20. $C_{28}H_{14}O_2(O{\cdot}CH_3)_2$ requires C = 81·08; H = 4·50 per cent.].

This *dimethoxy*-compound readily yields oxonium salts. Thus with ferric and stannic chlorides respectively in the presence of boiling acetic acid both the *ferrichloride* and *stannichloride* separate as minute, brown needles. These compounds, which are readily decomposed by water, could not be analysed owing to lack of material.

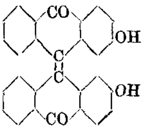
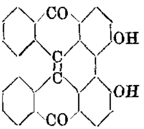
This compound, $C_{28}H_{16}O_4$, is identical with the substance previously obtained by the oxidation of 3 : 3′-dihydroxydianthrone (V) (Perkin and Whattam, *loc. cit.*) with permanganate :

(V.)



* For the isolation of this product from the brown, resinous product (*A*), the latter was digested with acetic anhydride and a trace of pyridine at the boiling point, the solution poured into water, the precipitate washed, dried, and extracted with boiling alcohol, by which a considerable amount of brown matter was undissolved. The extract on evaporation yielded crystals, and these, after washing with acetone, were recrystallised first from benzene and then from acetic acid. The substance *D* was absent in this case.

There can be little doubt that it consists of 2 : 2′-dihydroxydianthraquinone (VI). The only alternative formula is that of a dihydroxyhelianthrone (VII), and this for numerous reasons appears to be unlikely.

(VI.)   (VII).

The sparingly soluble acetyl compound (*D*) obtained during the isolation of the diacetyldianthraquinone was recrystallised from much benzene (Found: C = 77·4; H = 3·7 per cent.). It consisted of fine, yellow needles which decomposed before melting, becoming black at about 300°. It dissolved in sulphuric acid with a fine crimson colour, and from this solution, after keeping, cautious addition of acetic acid caused the deposition of maroon-coloured needles. These, which appeared to consist of an oxonium sulphate, became orange-red on treatment with water and then gave C = 80·81; H = 3·09 per cent. This compound is not dissolved by sodium hydroxide solution, an insoluble red sodium compound being thus produced. It does not melt below 320°.

The analytical figures suggest that this substance is closely allied to the 2 : 2′-dihydroxydianthraquinone described above, and may possess the formula $C_{28}H_{14}O_4$, that is, that it contains two hydrogen atoms less than the latter compound. Although it is possibly a helianthrone derivative, the amount produced has been too small for its detailed investigation.

Interesting was the fact that the dihydroxydianthraquinone and the substance $C_{28}H_{14}O_4$ could only be found in the dextrose–alkali fusion product when stick potassium hydroxide had been employed. This was apparently due to a trace of potassium nitrate in the latter, for when a mixture of the ordinary commercial alkali with potassium nitrate was employed, a positive result was obtained. In the absence of the oxidising agent, acetylation of the resinous matter yielded, according to the method described above, an acetyl compound crystallising in colourless needles melting at 302—303°. This apparently possesses the formula $C_{28}H_{14}O_4(C_2H_3O)_4$ (Found: C = 73·25; H = 4·34: acetic acid = 40·73 per cent.), and although very similar to the acetylated 3 : 3′-dihydroxydianthranol of Perkin and Whattam (*loc. cit.*), does not seem to be identical with this substance. A molecular weight determination gave *M* = 602. Its further investigation will be attempted.

In view of the behaviour of 2-hydroxyanthraquinone in these circumstances, other hydroxyanthraquinones, namely, erythroxyanthraquinone, anthraflavic acid, *iso*anthraflavic acid, alizarin, purpurin, and purpuroxanthin, have all been submitted to preliminary experiment under these conditions. Of these, only the anthraflavic acids have given up to the present compounds which appear to contain the benzanthrone nucleus. They closely resemble the above-described hydroxybenzanthronecarboxylic acid in appearance and properties, and when sufficient raw material is available, their preparation in large quantity will be undertaken.

Summary.

When 2-hydroxyanthraquinone is heated under pressure with dextrose, erythritol, glycerol, mannitol, or lævulose, hydroxybenzanthronecarboxylic acid (III) is formed together with a brown, amorphous substance, the latter being the main product of the reaction. Small amounts of 2 : 2′-dihydroxydianthraquinone (V) and of two compounds, $C_{28}H_{14}O_4$ and $C_{28}H_{18}O_4$, the nature of which is as yet uncertain, are simultaneously produced.

We are much indebted to the British Dyestuffs Corporation, Ltd., for many facilities for carrying out this work and for the supply of raw materials necessary for this purpose.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, March* 17*th*, 1922.]

CVI.—*Researches on Residual Affinity and Co-ordination. Part VIII. Interaction of Tellurium Tetrachloride and β-Diketones.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

OF seventy-seven elements possessing chemical properties no fewer than fifty-seven have been shown to yield with acetylacetone derivatives containing a univalent radicle $C_5H_7O_2'$. These products have in part been classified in an earlier communication (T., 1920, **117**, 1456), and a summary, already rendered incomplete by subsequent researches, is given of their properties, in "Beilstein's Handbuch" (edition 1918, vol. I, pp. 781—784).

On condensing acetylacetone with the tetrachlorides of selenium and tellurium we have obtained evidence that this β-diketone gives rise to a bivalent radicle $C_5H_6O_2''$, the condensation taking a

different course from the reactions hitherto recorded with the other elements.

The singular behaviour of the tetrachlorides of selenium and tellurium towards acetylacetone has now been examined more closely and our investigations have been extended to other β-diketones in order to find an explanation for the nature of this exceptional condensation. In the present communication, we deal with the case of tellurium tetrachloride, the reactions of which with acetylacetone and benzoylacetone have already received attention (*loc. cit.*; T., 1921, **119**, 611).

A detailed examination of the condensation between tellurium tetrachloride and acetylacetone in chloroform B.P. shows that three products are obtained which represent the three different types of compounds formed in the condensation of this tetrachloride and the other β-diketones. These typical substances from acetylacetone have the following molecular formulæ :

i. $(C_5H_7O_2)_2TeCl_2$. ii. $C_5H_6O_2{:}TeCl_2$. iii. $C_5H_6O(O{\cdot}C_2H_5)TeCl_3$.

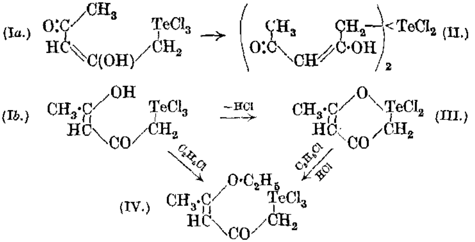
Tellurium bisacetylacetone dichloride, the first product (i) containing a univalent radicle $C_5H_7O_2'$, may be regarded as representing the normal condensation, yet it will be shown below that this univalent group is in all probability not identical but isomeric with the organic complexes present in metallic acetylacetones.

Tellurium acetylacetone dichloride (ii) contains the new bivalent radicle (T., 1920, *ibid.*), whereas the third compound, tellurium *O*-ethylacetylacetone trichloride (iii) arises from the intervention of ethyl chloride formed during condensation from the alcohol present in chloroform B.P.

The other β-diketones containing an acetyl group furnish tellurium derivatives conforming to one or other of the preceding types, but of the examples so far studied only acetylacetone gives rise to all three products. These practical results are explicable on the view that tellurium tetrachloride reacts initially with the terminal methyl group of the β-diketone, the subsequent course of the condensation depending on the enolic condition of the reactive primary product.

I. *Tellurium Tetrachloride and Acetylacetone.*

The initial reaction between these reagents proceeds with elimination of hydrogen chloride to the following primary product, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ (I), which, although not isolated, may be regarded as the parent substance of the three stable tellurium derivatives subsequently produced. Enolisation of the primary product leads alternatively to the forms *Ia* and *Ib*.



In the former condition (*Ia*), there is no tendency for the molecule to lose hydrogen chloride, since this condensation would lead to the formation of a highly strained, four-membered ring joining tellurium and the enolic oxygen, and accordingly condensation occurs with a second molecule of acetylacetone, leading to the production of tellurium bisacetylacetone dichloride (II). This compound retains the enolic properties of acetylacetone and gives characteristic ferric and copper derivatives. Hence the univalent *acetylacetone radicle, $C_5H_7O_2'$, present in this tellurium derivative* is essentially different from the isomeric complex in such metallic acetylacetones as the aluminium, gallium, and copper compounds.

Owing to the spatial arrangement of the molecule in the alternative enolisation (*Ib*) of the primary product I, the enolic group becomes adjacent to the tellurium radicle, $TeCl_3$, and, in pure chloroform, elimination of hydrogen chloride occurs with the production of tellurium acetylacetone dichloride (III) owing to the general tendency to form six-membered rings. If, however, ethyl chloride is either added or present as an impurity in the solvent, then ethylation of the enolic group occurs with the formation of tellurium *O*-ethylacetylacetone trichloride (IV), this product also arising from the joint action of hydrogen chloride and ethyl chloride on tellurium acetylacetone dichloride.

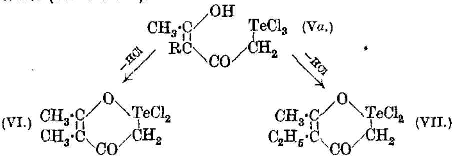
2. *Tellurium Tetrachloride and the 3-Alkylacetylacetones.*

The condensation between tellurium tetrachloride and *C*-methylacetylacetone or *C*-ethylacetylacetone takes a simple course, only one product being obtained in either case, namely, *tellurium 3-methylacetylacetone dichloride* (VI) or *tellurium 3-ethylacetylacetone dichloride* (VII), respectively.

In these instances the reactive primary product,

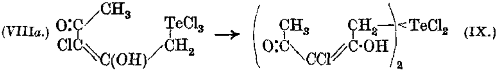
$$CH_3{\cdot}CO{\cdot}CHR{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3 \text{ (V)},$$

enolises on the side remote from the tellurium radicle to the modification V*a*, from which hydrogen chloride is eliminated readily owing to the tendency to form six-membered cyclic systems, thus leading to the production of the two *tellurium 3-alkylacetylacetone dichlorides* (VI and VII).



3. *Tellurium Tetrachloride and 3-Chloroacetylacetone.*

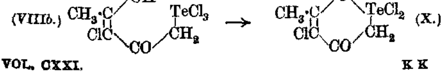
In the condensation between the tetrachloride and 3-chloroacetylacetone two substances are obtained corresponding with types i and ii. The main product is *tellurium bis-3-chloroacetylacetone dichloride* (IX), the by-product being *tellurium 3-chloroacetylacetone dichloride* (X). This result is explicable on the same general hypothesis; the formation of a reactive primary product, $CH_3 \cdot CO \cdot CHCl \cdot CO \cdot CH_2 \cdot TeCl_3$ (VIII), which then enolises into one or other of two modifications VIII*a* and VIII*b*.



The enolic form VIII*a* condenses with a second molecular proportion of 3-chloroacetylacetone to yield tellurium bis-3-chloroacetylacetone dichloride, which retains two enolic groups, as is shown by the production of copper tellurium bis-3-chloroacetylacetone dichloride.

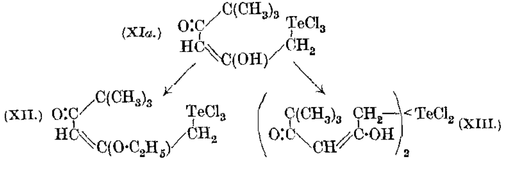
The formation of tellurium bis-3-chloroacetylacetone dichloride (IX), an enolic substance yielding metallic derivatives, is a crucial proof of the general hypothesis that tellurium becomes attached initially to a terminal methyl group. The alternative possibility of replacing the hydrogen of the chloromethylene group would not give rise to an enolic compound.

Owing to the spatial arrangement of the groups in the second enolic form, VIII*b*, the enolic and tellurium radicles become neighbours, so that hydrogen chloride is eliminated between them with the formation of *tellurium-3-chloroacetylacetone dichloride* (X).



4. *Tellurium Tetrachloride and Pivalylacetone (Acetylpinacolin).*

The interaction between the tetrachloride and pivalylacetone in chloroform B.P. leads to the formation of two compounds; the main product is *tellurium* O-*ethylpivalylacetone trichloride* (XII), the by-product being *tellurium bispivalylacetone dichloride* (XIII). It is evident by the absence of a cyclic compound (type i, page 923) that in this instance enolisation of the primary product $(CH_3)_3C{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ (XI) has occurred on the side remote from the tertiary butyl group. This mode of enolisation (XI*a*) inhibits any formation of a six-membered ring and tends either to ether formation (XII) or to condensation with a second molecule of pivalylacetone to tellurium bispivalylacetone dichloride (XIII).



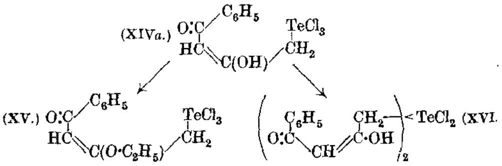
5. *Tellurium Tetrachloride and Benzoylacetone* (T., 1921, **119**, 617)

In this condensation using chloroform B.P. only two product are obtained, *tellurium bisbenzoylacetone dichloride* (XVI) an tellurium *O*-ethylbenzoylacetone trichloride (XV). This practica result can be explained on the basis of the same hypothesis as tha employed in the preceding condensation.

The primary product is the reactive compound

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$$

(XIV), which enolises only on the side remote from the phenyl grou to give the enolic modification XIV*a*.



When ethyl chloride is present etherification of the primar enolic compound takes place readily and tellurium *O*-ethylbenzoyl acetone trichloride (XV) results. In the absence of ethyl chlorid

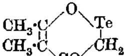
the primary product condenses with another molecule of benzoylacetone and tellurium bisbenzoylacetone dichloride results. This compound is enolic and yields a copper derivative.

The condensation was repeated in pure chloroform free from alcohol or ethyl chloride in the hope of producing a cyclic compound of type i (page 923), but in vain, the only derivative obtaiued was the bisbenzoylacetone compound (XVI), thus showing that enolisation of the primary product occurs on the side remote from the phenyl group.

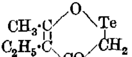
This summary of the experimental evidence obtained with six β-diketones shows that the condensations are capable of simple explanation on a general hypothesis. All the β-diketones examined contain a methyl group and at least one hydrogen atom attached to the central carbon atom situated between the two carbonyl groups. It is therefore evident that the four β-diketones, acetylacetone and its 3-alkyl and 3-halogen derivatives, which yield cyclic tellurium compounds (type *i*), contain each a bivalent radicle having the general formula $\underset{1}{-CH_2}\cdot \underset{2}{CO}\cdot \underset{3}{CX}{:}\underset{4}{CR}\cdot O-$. In this unsaturated group, which is obtained by eliminating one hydrogen from a terminal methyl group (1) and the other from an enolic group attached to carbon atom 4 of the chain, R may be either CH_3 or $CH_2\cdot CH_3$, whereas X represents a halogen atom or an alkyl group.

(XVII.) (XVIII.)

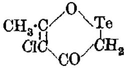
On reduction with sulphurous acid or alkali bisulphites the cyclic compounds of the general formula XVII are converted into cyclic organic derivatives, XVIII, of bivalent tellurium. This series includes *tellurium 3-methylacetylacetone* (XIX), *tellurium 3-ethylacetylacetone* (XX), and *tellurium 3-chloroacetylacetone* (XXI).



(XIX.)



(XX.)



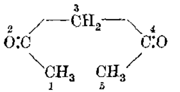
(XXI.)

These compounds, which resemble tellurinm acetylacetone in containing bivalent radicles of the general formula $C_5H_5XO_2''$, have a pronounced yellow colour and are sparingly soluble in water; their aqueous solutions exhibit a very marked inhibitory action on the growth of bacteria.

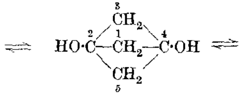
Further contributory evidence as to the validity of the formulæ for the foregoing tellurium derivatives is derived from the fact that

dibenzoylmethane, which contains no methyl group, does not condense with tellurium tetrachloride to yield a stable organic derivative; the crystalline yellow compound, $(C_6H_5{\cdot}CO)_2CH{\cdot}TeCl_3$, produced is readily decomposed by water into the original diketone and hydrochloric and tellurous acids.

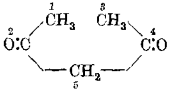
It should be pointed out that the reasoning employed in the foregoing discussion on the constitutional formulæ of the tellurium derivatives of the β-diketones is subject to an ambiguity inherent in the conventional representation of the chemical structure of these diketones. This uncertainty is due to the possibility of either simple or twofold enolisation arising from a migration of hydrogen from the terminal methyl groups. A molecule of diketonic acetylacetone (I) undergoing this change would pass into the dienolic form (II) and this labile modification might revert to the diketo-form (III) in such a way that one of the terminal carbon atoms 1 or 5 would take up the median position formerly occupied by the methylene carbon atom 3, the latter becoming the centre of a terminal methyl group.



(I.)



(II.)



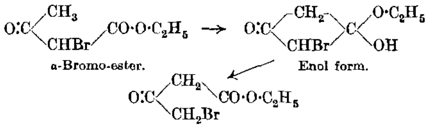
(III.)

If at any stage of these reversible changes the hydrogen attached to carbon atoms 1, 3, or 5 had undergone replacement by some other radicle, then it is obvious that the foregoing transformations would alter completely the orientation of the substituent.

Such otherwise inexplicable changes have been noticed, as for instance, in the progressive chlorination of acetylacetone, where one intermediate compound is the non-enolic 3 : 3′-dichloroacetylacetone, $CH_3{\cdot}CO{\cdot}CCl_2{\cdot}CO{\cdot}CH_3$, which by further treatment with chlorine gives 1 : 1′ : 1″ : 5 : 5′ : 5″-hexachloroacetylacetone, $CCl_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CCl_3$, the latter product justifying its constitution by hydrolysing into *as*-trichloroacetone, $CCl_3{\cdot}CO{\cdot}CH_3$, and trichloroacetic acid (Combes, *Ann. Chim. Phys.*, 1897, [vi], **12**, 237).

The transformation of ethyl α-bromoacetoacetate into ethyl γ-bromoacetoacetate observed by Hantzsch (*Ber.*, 1894, **27**, 356,

3168) can also be explained by the transitory formation of the cyclic enolic compound owing to enolisation from the terminal methyl group.



α-Bromo-ester. Enol form.

γ-Bromo-ester.

Subject to the ambiguity resulting from the foregoing enolic possibilities, the chemical constitutions ascribed to the tellurium derivatives of the β-diketones offer a general explanation of their chemical behaviour and mode of formation.

EXPERIMENTAL.*

I. *Interaction of Tellurium Tetrachloride and Acetylacetone in Alcohol-free Chloroform.*

In certain of the earlier experiments on this interaction in chloroform B.P. it was noticed that in addition to tellurium acetylacetone dichloride (III) and tellurium *O*-ethylacetylacetone trichloride (IV) there were indications of the presence of a third substance, *tellurium bisacetylacetone dichloride* (II), which, however, was separated with difficulty from the other products owing to its tendency to remain as a syrup in the final chloroform mother-liquor.

The problem of isolating this more elusive derivative has now been simplified by the employment of chloroform purified through the salicylide process, a procedure which eliminates alcohol and ethyl chloride from the solvent.

Eight grams of tellurium tetrachloride and 6 grams of acetylacetone in 90 c.c. of "salicylide" chloroform were heated under reflux for forty-five minutes, when the tetrachloride had dissolved with the separation of a small amount of tellurium. The orange solution was concentrated to about 40 c.c., filtered, and evaporated in a vacuum; the yellow syrup stirred with a small amount of chloroform was allowed to crystallise, when 2·7 grams of tellurium acetylacetone dichloride separated (yield 30 per cent.). The filtrate was shaken with a few c.c. of water, when 0·6 gram of tellurium dioxide was removed; the chloroform filtrate was then left to evaporate completely, when the semi-solid residue, spread on porous tile, yielded 2·0 grams of tellurium bisacetylacetone

* We wish to express our cordial thanks to Mrs. Campbell Brown and Professor Collie for a valuable gift of tellurium.

dichloride (yield 18 per cent.). When recrystallised from benzene, this compound separated in colourless, silvery flakes melting and blackening at 115° (Found: C = 30·51; H = 3·66; Cl = 17·94; Te = 32·61. $C_{10}H_{14}O_4Cl_2Te$ requires C = 30·27; H = 3·56; Cl = 17·88; Te = 32·15 per cent.).

When dissolved in chloroform and treated with aquo-alcoholic ferric chloride, tellurium bisacetylacetone dichloride gave instantly a blood-red coloration. It dissolved only sparingly in cold alcohol bnt decomposed in the hot solvent; it remained unchanged in boiling chloroform.

Tellurium acetylacetone arising from the foregoing dichloride (III) has again been examined; it was found to melt more sharply at about 182° than was formerly recorded (T., 1920, *ibid.*, gave m. p. 145—182°). When treated with dilute hydriodic acid, tellurium *acetylacetone yielded tellurium, acetylacetone, and tellurium* acetylacetone di-iodide (the purple variety, *loc. cit.*).

II. *Interaction of Tellurium Tetrachloride and Benzoylacetone in Alcohol-free Chloroform.*

In chloroform containing alcohol, tellurium tetrachloride and benzoylacetone had given an 80 per cent. yield of pure tellurium *O*-ethylacetylacetone trichloride (T., 1921, *ibid.*, 617). By the use of chloroform deprived by the salicylide process of all but the merest trace of alcohol it was expected that this ethyl derivative would not be formed. This anticipation was verified.

To 4 grams of tellurium tetrachloride in 40 c.c. of "salicylide" chloroform were added 4·8 grams of purified benzoylacetone (2 mols.). The tetrachloride dissolved rapidly in the cold to a pale yellow, turbid solution, which was heated under reflux for seventy-five minutes; hydrogen chloride was evolved; the dark reddish-brown solution was filtered from traces of tellurium and the chloroform evaporated under reduced pressure. The gummy product was extracted with light petroleum to remove unchanged benzoylacetone and with chloroform and water to separate tellurium dioxide, the product passing into the organic solvent. The semi-solid residue obtained by removing the chloroform dried to a brown, flaky mass of *tellurium bisbenzoylacetone dichloride* (XVI) mixed with benzoylacetone, the latter being extracted by light petroleum (total weight recovered, 1 gram). The dichloride, when crystallised from dry ethyl acetate, was obtained in well-defined, flattened, yellowish white needles melting and blackening at 148° (Found: C = 46·51; H = 3·61; Cl = 13·93; Te = 24·28. $C_{20}H_{18}O_4Cl_2Te$ requires C = 46·11; H = 3·48; Cl = 13·62; Te = 24·49 per cent.). Tellurium bisbenzoylacetone dichloride was insoluble in water or

light petroleum; it dissolved sparingly in cold benzene, chloroform or ethyl acetate, and more readily in the hot solvent or in acetone. With aquo-alcoholic ferric chloride it gave instantly a red coloration.

When using the reagents in molecular proportions in order to facilitate if possible the production of a tellurium derivative containing the bivalent radicle $C_{10}H_8O_2''$, this hypothetical product was not obtained, but the final residues, when extracted successively with light petroleum and carbon tetrachloride, left a residue (0·5 per cent.) of *O*-ethylbenzoylacetone trichloride (XV) which was identified against an analysed specimen of this compound (C = 33·73; H = 3·27. $C_{12}H_{13}O_2Cl_3Te$ requires C = 34·05; H = 3·10 per cent.).

III. *Action of Tellurium Tetrachloride on 3-Alkylacetylacetones.*

Tellurium 3-Methylacetylacetone Dichloride (VI).—Tellurium tetrachloride (8·9 grams) in 100 c.c. of chloroform B.P., when treated with 7·6 grams (2 mols.) of redistilled *C*-methylacetylacetone in 25 c.c. of the same solvent, speedily dissolved to a dark reddish-brown solution, which was then heated under reflux for one hour, hydrogen chloride being evolved. *Tellurium 3-methylacetylacetone dichloride*, which separated, mixed with 0·2 gram of free tellurium, was extracted with cold acetone, recovered in crystalline form by evaporation, and added to the main chloroform solution, when crystallisation set in and continued for several days, the solution being left in a vacuum desiccator. The total yield of dichloride obtained in two crops was 6·8 grams (67 per cent.); no other tellurium derivative was noticed and a considerable amount of unchanged *C*-methylacetylacetone was detected. Tellurium 3-methylacetylacetone dichloride separated from acetone in stout, hexagonal needles or prisms having obliquely truncated ends. It was colourless when highly purified but generally of a brownish-grey tint owing to traces of tellurium. It was only sparingly soluble in water or in organic solvents other than acetone. At 180° it became discoloured and changed to a black mass at 190°. In this absence of definite melting point it resembled its *C*-ethyl homologue and differed from tellurium acetylacetone dichloride and tellurium chloroacetylacetone dichloride (Found: C = 23·19; H = 3·02; Cl = 23·30; Te = 40·67. $C_6H_8O_2Cl_2Te$ requires C = 23·20; H = 2·60; Cl = 22·84; Te = 41·06 per cent.).

Tellurium 3-Methylacetylacetone (XIX).—To 4·3 grams of finely ground tellurium 3-methylacetylacetone dichloride mechanically stirred in 20 c.c. of ice cold water were added slowly 6·1 grams (≡ 4 mols. $KHSO_3$) of powdered potassium metabisulphite; sulphur

dioxide was evolved and after thirty minutes the yellow product containing only a trace of free tellurium was removed and crystallised successively from hot water and benzene: yield 2·5 grams or 76 per cent. of theory.

Tellurium 3-methylacetylacetone crystallised in small, hexagonal, pale golden-yellow plates often acicular in habit. It dissolved sparingly in hot water, more readily in boiling benzene or cold chloroform. It darkened from 155° and decomposed sharply at 170° with separation of tellurium; it was more stable on heating than tellurium acetylacetone (T., 1920, **117**, 1464) and sublimed at 140° in a vacuum to small, compact, yellow prisms. It was non-enolic towards ferric and cupric salts and it possessed little residual acidity, being comparatively insoluble in cold 5*N*-sodium hydroxide, whereas tellurium acetylacetone (*loc. cit.*) dissolved at once; the yellow solutions of these two tellurium derivatives were unstable, rapidly depositing the metalloid. The monomeric nature of tellurium 3-methylacetylacetone was demonstrated by molecular weight determination in boiling benzene ($k = 25{\cdot}7$, $c = 1{\cdot}001$). $M = 243$ (Found: C = 29·89; H = 3·57; Te = 52·92. $C_6H_8O_2Te$ requires C = 30·06; H = 3·36; Te = 53·22 per cent.; $M = 239{\cdot}5$). This compound contained tellurium in the bivalent condition and combined additively with bromine or iodine in cold 2 per cent. chloroform solution.

Tellurium 3-methylacetylacetone dibromide, $(C_5H_5O_2{\cdot}CH_3){:}TeBr_2$, when obtained in quantitative yield by the direct union of its generators in molecular proportions, was precipitated in pale yellow crystals and separated from alcohol in yellowish-white prisms melting with decomposition and violent intumescence at 152—153° (Found: Br = 39·61. $C_6H_8O_2Br_2Te$ requires Br = 40·02 per cent.).

Tellurium 3-methylacetylacetone di-iodide, $(C_5H_5O_2{\cdot}CH_3){:}TeI_2$, a crimson, crystalline powder, sintering sharply at 134° to a black core which intumesced at 175—176°; recrystallised from alcohol or ethyl acetate, it formed reddish-purple crystals sintering and intumescing at appreciably lower temperatures, these changes occurring at 131—134° and at 169—171° respectively (Found: I = 51·03. $C_6H_8O_2I_2Te$ requires I = 51·44 per cent.).

Tellurium 3-Ethylacetylacetone Dichloride (VII).—To 9·0 grams of tellurium tetrachloride in 100 c.c. of chloroform B.P. were added 8·5 grams (2 mols.) of redistilled *C*-ethylacetylacetone. The tetrachloride dissolved in the cold to a dark orange-yellow solution, which was then heated under reflux for forty-five minutes, hydrogen chloride being evolved. *Tellurium 3-ethylacetylacetone dichloride*, which then separated, was contaminated with free tellurium and

an oily by-product; it was extracted with cold acetone and recovered in a crystalline form (2 grams). The main chloroform filtrate on spontaneous evaporation furnished 6·6 grams of glistening crystals of the dichloride (total yield 80 per cent.). This product was homogeneous, no other tellurium derivative being detected. Tellurium 3-ethylacetylacetone dichloride resembled its lower homologues in solubility, dissolving readily in acetone, more sparingly in other organic media such as chloroform or the alcohols. Colourless when pure, it generally had a brown tinge and separated from acetone or hot methyl alcohol in highly lustrous, hexagonal prisms having no definite melting point but blackening at 185—190°. It gave no coloration with aquo-alcoholic ferric chloride and was decomposed by prolonged heating with alcohol (Found: C = 25·75; H = 3·29; Cl = 21·98; Te = 39·68. $C_7H_{10}O_2Cl_2Te$ requires C = 25·90; H = 3·11; Cl = 21·85; Te = 39·29 per cent.). When inhaled in the form of dust, this dichloride has an extremely irritating action on the mucous membrane of the nostrils.

Tellurium 3-ethylacetylacetone dichloride dissolved to a yellow solution in chloroform B.P. saturated with hydrogen chloride, but underwent no further change even on adding ethyl chloride. On evaporating off the solvent the dichloride was recovered. Even after prolonged boiling there was no sign of esterification but only a partial decomposition as follows:

$$(C_5H_5O_2\cdot C_2H_5)\colon TeCl_2 + 2HCl = TeCl_4 + C_5H_7O_2\cdot C_2H_5.$$

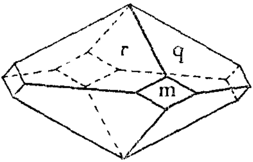
Tellurium 3-Ethylacetylacetone (XX).—Tellurium 3-ethylacetylacetone dichloride (3·3 grams) stirred into 85 c.c. of water at 0° was reduced by the gradual addition of 4·5 grams of potassium metabisulphite (4 mols. $KHSO_3$). There was but little liberation of tellurium and after thirty minutes the yellow product was crystallised from boiling water, when 2·3 grams (88 per cent.) of purified *tellurium 3-ethylacetylacetone* were obtained [Found: M in boiling toluene (k = 33·8, c = 2·450) = 260. C = 32·91; H = 4·07; Te = 50·59. $C_7H_{10}O_2Te$ requires C = 33·14; H = 3·98; Te = 50·27 per cent.; M = 253·5].

Tellurium 3-ethylacetylacetone separated from hot water or alcohol in odourless, yellow needles or more compact prisms and from benzene in lustrous, primrose-yellow, hexagonal leaflets. It dissolved readily in cold chloroform and, like its lower methyl homologue, was much more soluble in benzene than is tellurium acetylacetone. Its aqueous solution was neutral and showed no enolic properties; it was almost devoid of residual acidity, thus differing from tellurium acetylacetone or tellurium 3-chloroacetylacetone in its sparing solubility in cold $5N$-sodium hydroxide

or in aqueous sodium carbonate. It blackened in contact with the former alkali, although showing great stability towards moist or dry heat. Unlike tellurium acetylacetone, it withstood prolonged boiling with water and in a vacuum it sublimed slowly but completely at 130° in long needles which became transformed as the temperature rose to 140° into small, yellow, prismatic crystals melting at 142° to a transparent, yellow liquid from which black tellurium separated on heating at 160°.

The crystals were kindly examined by Mr. T. V. Barker, who reports as follows. Although exceedingly small (the greatest dimension being 0·4 mm.), measurement on the two-circle goniometer presented no difficulty. The system was first thought to be tetragonal, but a subsequent optical examination showed that, however tetragonal geometrically, the crystals really represent an orthorhombic combination of $q\{011\}$, $r\{101\}$, and $m\{110\}$, as shown in Fig. 1. The axial ratios, $a:b:c = 1:1:0·7221$, follow from the annexed values, representing the mean results of measurement of two crystals:

FIG. 1.



Tellurium *C*-ethylacetylacetone dichloride.

	$m(110)$.	$q(011)$.	$r(101)$.
Azimuth (ϕ)	45° 0′	0° 0′	90° 0′
Polar Distance (ρ)	90 0	*35 50	*35 50

Fedorov complex-symbol, 4*o* (45° 36′) ± 0. Optically the crystals are biaxial; the acute bisectrix is negative.

Tellurium 3-Ethylacetylacetone Dihaloids.—The dichloride was regenerated in almost colourless crystals from the preceding compound on passing dry chlorine into its chloroform solution.

Tellurium 3-ethylacetylacetone dibromide, $(C_5H_5O_2·C_2H_5)$:$TeBr_2$, obtained quantitatively on mixing chloroform solutions of tellurium 3-ethylacetylacetone and bromine at 0°, separated from methyl or ethyl alcohol in lustrous, very pale yellow crystals, non-enolic towards ferric chloride. Various preparations intumesced with liberation of tellurium over a temperature range of 161—170° (Found: Br = 38·54. $C_7H_{10}O_2Br_2Te$ requires Br = 38·66 per cent.).

Tellurium 3-ethylacetylacetone di-iodide, $(C_5H_5O_2·C_2H_5)$:TeI_2, separated quantitatively in reddish-orange crystals from its generators in chloroform solution and crystallised from ethyl alcohol in light scarlet crystals. In powdered form and in alcoholic solutions

its colour was orange; it gave no coloration with aquo-alcoholic ferric chloride. It sintered and blackened at 149° and decomposed with intumescence at 176° (Found: I = 50·01. $C_7H_{10}O_2I_2Te$ requires I = 50·02 per cent.).

IV. *Action of Tellurium Tetrachloride on Chloroacetylacetone.*

The chloroacetylacetone employed in the following experiments was the product arising from the action of selenium tetrachloride on acetylacetone. It was purified through its green copper salt and fractionated until of constant boiling point, being then a colourless, intensely lachrymatory oil boiling at 149—150°/750 mm. and giving an intensely red coloration with ferric chloride.

To 11 grams of tellurium tetrachloride suspended in 60 c.c. of chloroform B.P. (not dried) were added 11 grams (2 mols.) of chloroacetylacetone; a portion of the tetrachloride dissolved forthwith and the remainder disappeared on warming. When heated under reflux for one and three-quarter hours, the yellow solution evolved hydrogen chloride rapidly at first and then more slowly while the colour changed to dark brown. Very little tellurium was eliminated and the filtered liquid was evaporated to complete dryness in a vacuum; there was no separation of crystals at any stage, the gummy residue was dissolved in chloroform and evaporated under reduced pressure to a syrupy consistence to remove unchanged chloroacetylacetone. The syrup, left over solid sodium hydroxide, partly solidified. The mixture was stirred with cold chloroform, thus yielding a solid residue *a* (by-product) and a chloroform extract *b* (containing main product).

Tellurium Chloroacetylacetone Dichloride (X).—Residue *a* of the foregoing condensation was extracted with cold acetone, filtered from tellurium dioxide and elemental tellurium, and the filtrate left to evaporate, when brownish-white crystals of the dichloride were obtained (0·6 gram or 5 per cent.). It resembled its analogues from acetylacetone and the 3-alkylacetylacetones in being very sparingly soluble in chloroform and other volatile organic solvents with the exception of acetone. When purified, it separated in colourless crystals, usually, however, having a brown tinge; it melted and decomposed with intumescence at 161—162° (Found: Te = 39·05. $C_5H_5O_2Cl_3Te$ requires Te = 38·52 per cent.). Its constitution was determined by reduction to the following compound.

Tellurium Chloroacetylacetone (XXI).—One gram of powdered tellurium chloroacetylacetone dichloride was stirred continuously in 20 c.c. of ice cold water and reduced by the gradual addition of 1·3 grams of powdered potassium metabisulphite (4 mols. $KHSO_3$).

After thirty minutes the yellow product was extracted with boiling water, the solution filtered from tellurium and allowed to crystallise, when pale golden-yellow needles of *tellurium chloroacetylacetone* were obtained (0·4 gram or 51 per cent.); this compound also separated from hot benzene in voluminous masses of light yellow needles; it blackened and decomposed sharply at 153—154°. Tellurium chloroacetylacetone is the least soluble member of this series of tellurium compounds either in water or in organic media.

The aqueous solution of tellurium chloroacetylacetone was distinctly acidic to litmus but non-enolic towards ferric chloride. It dissolved in aqueous sodium carbonate to a yellow solution stable in the cold but blackening on boiling; it was less soluble in aqueous sodium bicarbonate, but dissolved immediately in cold 5*N*-sodium hydroxide, the cold solution being unstable and liberating tellurium. These properties show that tellurium chloroacetylacetone has residual acidity, thus resembling tellurium acetylacetone, the two compounds differing markedly in this respect from the tellurium 3-alkylacetylacetones (Found: Cl = 13·65. $C_5H_5O_2ClTe$ requires Cl = 13·64 per cent.).

Tellurium Bischloroacetylacetone Dichloride (IX).—The chloroform extract *b* from the condensation of chloroacetylacetone and tellurium tetrachloride evaporated to a dark glue which did not solidify completely on treatment with various organic solvents. Accordingly the semi-solid mass was spread on porous tile, when the oily portion drained away, leaving pale brown crystals (3·0 grams, yield 16 per cent.) of *tellurium bischloroacetylacetone dichloride*, which was recrystallised from ligroin (b. p. 80—100°) or from a mixture of carbon tetrachloride and light petroleum (b. p. 40—60°) and thus obtained in transparent, colourless, feathery, prismatic needles melting with blackening and decomposition at 131—132° (Found: C = 25·85; H = 2·90; Cl = 30·50; Te = 27·59. $C_{10}H_{12}O_4Cl_4Te$ requires C = 25·79; H = 2·60; Cl = 30·47; Te = 27·39 per cent.).

Tellurium bischloroacetylacetone dichloride, which was readily soluble in hot benzene or cold chloroform, dissolved more sparingly in ether; it was markedly enolic, giving forthwith a very intense red coloration with ferric chloride in aquo-alcoholic chloroform. When it was cautiously reduced with cold aqueous potassium hydrogen sulphite and the unstable yellow insoluble product warmed with water, black tellurium and chloroacetylacetone were produced. Even without reducing agent the compound underwent decomposition in boiling water, giving tellurium and chloroacetylacetone. With cold aqueous sodium hydroxide, hydrolysis occurred smoothly, leading to sodium tellurite and sodium chloroacetylacetone, the latter being identified as its green copper salt.

The oily portion of chloroform extract *b* did not yield any other definite product, so that the total yield of tellurium derivatives from *a* and *b* accounted for only about 21 per cent. of the calculated amount and no improvement was obtained by using chloroform B.P. freed from alcohol by washing with water and subsequently dried over calcium chloride. This result excludes to a large extent the possibility of esterification of tellurium chloroacetylacetone dichloride to an analogue of tellurium *O*-ethylacetylacetone trichloride. The dahlia-like odour of *O*-ethylacetylacetone noticeable on treating the residual syrups with cold aqueous sodium hydroxide was probably due to a trace of acetylacetone in the chloroacetylacetone.

V. *Action of Tellurium Tetrachloride on Pivalylacetone (Acetylpinacolin).*

Methyl *tert.*-butyl ketone (pinacolin), prepared by distilling 100 grams of pinacone with 1 litre of water and 80 c.c. of concentrated sulphuric acid, was salted out and dried with potassium carbonate and rectified by distilling at 104—108°. Pivalylacetone (acetylpinacolin), described by Couturier (*Compt. rend.*, 1910, **150**, 928), was prepared both by the dry sodium ethoxide and sodium processes, giving yields respectively of 12 and 25 per cent., so that the latter was adopted.

To 7·8 grams of sodium wire in 130 c.c. of dried ethyl acetate cooled in ice were added 34 grams of pinacolin. The sodium had disappeared within twelve hours but without deposition of sodium salt. On warming on the water-bath, the mixture became solid and after forty-five minutes the cooled mixture was treated with ice water. The ethyl acetate layer separated and was washed with water, the aqueous layers and washings, after partial neutralisation with acetic acid, being treated with cupric acetate, when the violet-blue copper salt was precipitated. This copper derivative sintered at 188° and melted at 190° to an intensely blue liquid which resolidified on cooling to a mass of crystals; it dissolved readily in cold organic solvents including absolute ether and sublimed in small, blue prisms completely without decomposition on heating in a vacuum. When heated at high temperatures in a test-tube, it gave a bright copper mirror. Pivalylacetone (acetylpinacolin), made by decomposing the copper salt with dilute sulphuric acid in presence of ether and purified by repeated fractionation, was obtained as a colourless, fragrant oil boiling at 170—171°/745 mm. (Couturier, *loc. cit.*, gives b. p. 168°).

Tellurium O-*Ethylpivalylacetone Trichloride* (*Tellurium* O-*Ethylacetylpinacolin Trichloride*).—To 3·2 grams of tellurium tetrachloride suspended in 35 c.c. of chloroform B.P. (undried) were added 3·4

grams of acetylpinacolin. The tetrachloride dissolved rapidly to a yellow solution, which was heated under reflux for one hour on the water-bath, rapid evolution of hydrogen chloride occurred, and the orange-yellow solution was decanted from a trace of dark oil and evaporated in a desiccator. Unchanged acetylpinacolin volatilised and was detected by its odour; the golden-yellow oil solidified to a mass of *pale yellow crystals*, which were dried on porous tile (*yield 3·8 grams*). The product was completely soluble in cold chloroform and hence contained no analogue of tellurium acetylacetone dichloride. It consisted mainly of *tellurium O-ethylpivalylacetone trichloride* (XII), which in the impure condition gave a red coloration with ferric chloride, due to a soluble enolic by-product, probably tellurium bispivalylacetone dichloride, but in this condensation with chloroform B.P. the amount was too small for detailed study.

After repeated crystallisation from ligroin or preferably from equal volumes of carbon tetrachloride and light petroleum (b. p. 40—60°) the trichloride was obtained in transparent, yellowish-white, prismatic needles sintering at 114° and melting at 116° to a liquid which rapidly blackened (Found: C = 29·52; H = 4·25; Cl = 26·11; Te = 31·83. $C_{10}H_{17}O_2Cl_3Te$ requires C = 29·78; H = 4·25; Cl = 26·39; Te = 31·63 per cent.).

Tellurium *O*-ethylpivalylacetone trichloride became distinctly yellow after dissolving in carbon tetrachloride and precipitating by light petroleum; it was very readily soluble in all organic media except in light petroleum. When pure, it was non-enolic towards ferric chloride, in this respect resembling its acetylacetone and benzoylacetone analogues. Cold aqueous sodium hydroxide or carbonate removed tellurium, leaving *O-ethylpivalylacetone* (*O-ethylacetylpinacolin*), a colourless oil with a powerful odour of caraway and pine cones.

Tellurium Bispivalylacetone Dichloride (*Tellurium Bisacetylpinacolin Dichloride*, XIII).—To 3·9 grams of tellurium tetrachloride suspended in 25 c.c. of pure alcohol-free chloroform were added 3·8 grams of acetylpinacolin, when the tetrachloride dissolved partly in the cold to a yellow solution containing a flocculent precipitate which disappeared on boiling under reflux. Hydrogen chloride was evolved and the orange-yellow liquid was darkened by the separation of black tellurium. After 2½ hours the filtered solution was concentrated under reduced pressure to a syrup which crystallised in part, the liquid portion containing unchanged reagents. The homogeneous crystals (1·6 grams), drained from the viscid syrup on porous tile and recrystallised from a mixture of carbon tetrachloride and light petroleum, separated in colourless,

glistening flakes melting with decomposition at 133° (Found: C = 39·51; H = 5·51; Cl = 15·13; Te = 27·02. $C_{16}H_{26}O_4Cl_2Te$ requires C = 39·96; H = 5·45; Cl = 14·75; Te = 26·52 per cent.).

Tellurium bispivalylacetone dichloride (XIII) was readily soluble in cold chloroform or ethyl acetate, dissolving less readily in carbon tetrachloride, and insoluble in light petroleum. It reacted at once with copper acetate and gave an immediate red coloration with ferric chloride. The dichloride depressed considerably the melting point of tellurium *O*-ethylpivalylacetone trichloride and differed from the latter in giving rise to no fragrant *O*-ether on treatment with cold 5*N*-sodium hydroxide.

VI. *Action of Tellurium Tetrachloride on Dibenzoylmethane.*

To 3 grams of tellurium tetrachloride suspended in 35 c.c. of alcohol-free chloroform were added 5 grams (2 mols.) of dibenzoylmethane. The latter reagent and part of the tetrachloride dissolved in the cold, a bright yellow powder being then precipitated. The mixture was subsequently heated under reflux for two hours, moisture being excluded; the yellow powder and the remaining tetrachloride soon dissolved, hydrogen chloride being evolved. A mass of bright yellow crystals separated during boiling and the yellow solution gave a further crop on concentration under reduced pressure. The final mother-liquor, evaporated to dryness, yielded 2 grams of unchanged dibenzoylmethane. Hence only one molecular proportion of diketone was used in forming the golden-yellow crystals. This product was very unstable and on a short exposure to the air it changed to a colourless mixture of tellurium oxychloride and dibenzoylmethane. This hydrolysis was also produced by moist organic solvents and especially cold acetone. Analysis of the unaltered crystals showed that these consisted of *tellurium dibenzoylmethane trichloride* (Found: Cl = 23·24; Te = 27·34. $C_{15}H_{11}O_2Cl_3Te$ requires Cl = 23·28; Te = 27·90 per cent.). This trichloride was insoluble in dry ether, sparingly so in cold chloroform, and dissolved more readily in hot dry benzene.

[With E. A. Cooper.]

Bactericidal Action of Tellurium Acetylacetone and its Homologues.

Dr. E. A. Cooper has kindly examined the action on *bacillus coli* of the four water-soluble compounds having the foregoing general formula XVIII (page 927) and his results show that the effect of these tellurium derivatives is much greater than that of the parent β-diketones, which have been previously shown to be only feebly bactericidal (Morgan and Cooper, *Biochem. J.*, 1921, **15**, 587).

Preliminary experiments indicated that the tellurium derivatives had very high carbolic coefficients, thus behaving as powerful germicides.

Tellurium derivative.	*Carbolic coefficient.*
Tellurium acetylacetone	680
Tellurium *C*(3)-methylacetylacetone	250
Tellurium *C*(3)-ethylacetylacetone	250
Tellurium propionylacetone*	2430
Tellurium 3-chloroacetylacetone	24

* This compound will be described in a subsequent communication.

On subculturing the broth tubes with fresh broth and on subsequent incubation it was found, however, that fresh growths occurred, thus showing that the bacilli had not really been destroyed but had only had their growth inhibited. To this extent the foregoing carbolic coefficients are fallacious, the results of subculture indicating that these tellurium derivatives are not true germicides but merely powerful growth inhibitors. The carbolic coefficients may nevertheless be taken as approximate measures of inhibitory power, and it is seen that this action diminishes as substitution proceeds in the 3-methylene group. The inhibitory power is much more depressed by the substitution of chlorine than by that of an alkyl group. This decrease is probably due to a diminution in solubility, tellurium 3-chloroacetylacetone being the least soluble member of the foregoing series.

Tellurium propionylacetone and tellurium 3-methylacetylacetone are isomeric derivatives, but the former, which contains the substituted methyl group attached to a terminal carbon atom, exhibits a far more powerful inhibitory action than tellurium acetylacetone itself. This propionyl derivative has, moreover, a further advantage in being much more freely soluble than the other tellurium compounds examined. It is estimated from the foregoing carbolic coefficient determinations that the soluble propionyl compound exerts a definite inhibitory effect in as low a concentration as 1 in 5,000,000. The possibilities of the therapeutic application of this compound should accordingly be thoroughly explored. It is obvious in the case of substances used internally that inhibitory power is quite as useful as germicidal efficacy, since in consequence of inhibition the number of micro-organisms remains relatively small, thus enabling the natural protective mechanism of the animal organism to become effective.

The authors desire to express their thanks to the Advisory Council for Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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CVII.—*Properties of Mixtures of Ethyl Ether, Sulphuric Acid, and Water.*

By James Robert Pound.

Some years ago, at the suggestion of Professor Masson, the author determined certain properties of mixtures of sulphuric acid and ethyl ether, and the similarity was pointed out between these binary mixtures and those of sulphuric acid and water (T., 1911, **99**, 698). This paper deals with certain properties of ternary mixtures of these substances and with the conclusions drawn therefrom, which are based on the commonly accepted theories of association and dissociation of liquid mixtures.

The densities, viscosities, and electrical conductivities at 30° of mixtures of ether and each of four sulphuric acid–water solutions have been measured, and the results correlated with those found for mixtures of ether and pure sulphuric acid at 30° (*loc. cit.*) and with those recorded by other observers for mixtures of sulphuric acid and water at the same temperature. The four aqueous sulphuric acids were made up from commercial acid of good quality, and the ternary mixtures from an aqueous acid and ether which had been specially purified and dried. The thermometer in the thermostat was standardised against a platinum resistance thermometer. The measurements were made with the usual precautions, and the results are given in the accompanying tables, the figures therein being all significant. The measurements are expressed in *C.G.S.* units; the contraction, *c*, is that which occurs on mixing *x* c.c. of ether, *y* c.c. of sulphuric acid, and $(100-x-y)$ c.c. of water, and therefore $(100-c)$ c.c. of mixture will be obtained. Since the three substances are not miscible in all proportions, there is a range of unattainable homogeneous mixtures.

The densities ($d_{4^\circ}^{30^\circ}$) of the sulphuric acid–water mixtures were taken from the mean values recorded in the Landolt-Bornstein Tabellen (1905); the specific conductivities at 30° were calculated from Kohlrausch's results at 18°, the temperature coefficients there given for the range 18—26° being applied up to the temperature 30°; and the viscosities at 30° were calculated from Dunstan and Wilson's results at 25° (T., 1907, **91**, 83; *Chem. News*, 1914, **109**, 209), using the mean value, 0·864, of $\eta_{30^\circ}/\eta_{25^\circ}$.

In this paper are considered the following six sets of mixtures of ether and (1) 100, (2) 98·25, (3*a*) 95·25, (3*b*) 95·0, (4) 84·10, (5) 49·77 per cent. (by weight) sulphuric acid, and of (6) water and 100 per cent. sulphuric acid. The data are tabulated at the end of the paper.

FIG. 1.

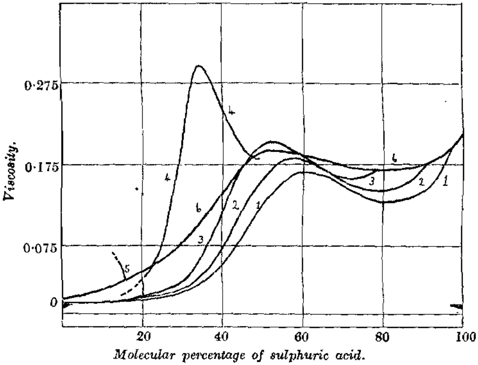
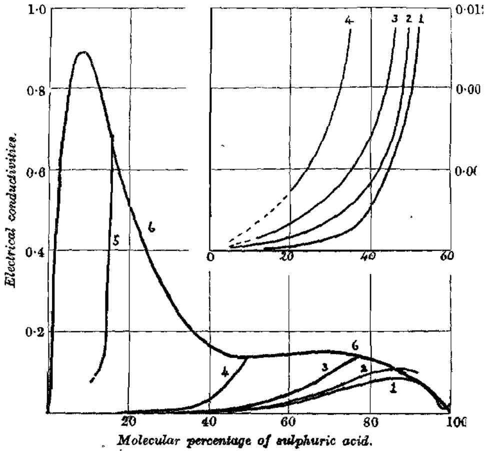
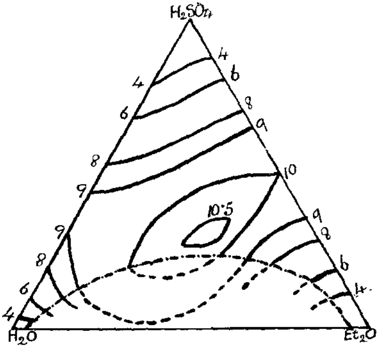

0·275
0·175
0·075
0
Viscosity.
20
40
60
80
100
Molecular percentage of sulphuric acid.

FIG. 2.


1·0
0·8
0·6
0·4
0·2
Electrical conductivities.
20
40
60
80
0
20
40
60
Molecular percentage of sulphuric acid.

In the figures showing the viscosity (Fig. 1) and the conductivity results (Fig. 2), the six curves follow the experiments closely; the abscissæ represent the molecular percentage of sulphuric acid in the mixtures, but in the curves (2) to (5) the ratio Et_2O/H_2O (by weight or by molecules) is increasing from 0 at the acid end (on curve 6) to ∞ at the ether end (on curve 1), although in each set of mixtures the ratio H_2SO_4/H_2O is constant. In Fig. 3 the contractions have been set to triangular co-ordinates; here the perpendicular distance from one side denotes the molecular percentage of one component, and the lines mark out mixtures of equal contractions.

FIG. 3.



Contraction occurring on mixing ethyl ether, sulphuric acid, and water.

The changes in density and in viscosity that occur with the formation of these ternary mixtures are consistent with (1) dissociation of the complex molecules, at the least $(H_2SO_4)_2$, which are present in pure sulphuric acid, and (2) the formation of various dissociable complexes such as H_2SO_4,H_2O, H_2SO_4,Et_2O, $H_2SO_4,2Et_2O$, $H_2SO_4,2H_2O$, and H_2SO_4,H_2O,Et_2O. The first three complexes have been isolated; by freezing-point and heat of mixing data other observers have substantiated the existence in solution of the first four complexes; and now the present data indicate with certainty the existence in solution of the ternary complex, the mixtures containing the three components in approximately equimolecular proportions are those having the greatest viscosity and are also those formed with the greatest contraction on mixing.

The *interpretation* of the conductivity–composition curves must await further knowledge of the conductivity of concentrated solutions in general. There are, as the conductivities show, striking differences between ethereal and aqueous solutions of sulphuric acid, and no simple relation exists between the conductivities of these mixtures and the composition of the complexes the presence of which has been indicated by other methods of investigation.

TABLE I.

Ether. Wt. %.	$d_{4°}^{30°}$.	Contraction (c.c.).	Viscosity. $\eta\times10^3$.	Conductivity. $\kappa\times10^3$.	Ether. Wt. %.	$d_{4°}^{30°}$.	Contraction (c.c.).	Viscosity. $\eta\times10^3$.	Conductivity. $\kappa\times10^3$.
Mixtures of Ether and 98·25(wt.)% H_2SO_4 at 30°.									
100	0·7021	0	2·134	0·000	30·360	1·34478	9·39	178·1	28·32
78·605	0·85227	5·33	5·676	0·376	22·033	1·45422	8·16	159·3	50·12
58·835	1·02984	9·02	29·02	1·953	13·884	1·57435	6·22	140·5	82·77
53·850	1·07857	9·54	50·70	2·670	8·9375	1·65737	4·93	140·7	100·7
48·056	1·13897	9·83	93·2	4·61	5·383	1·72127	3·67	148·2	109·2
41·853	1·20732	9·93	144·4	9·24	1·885	—	—	—	107·0
35·022	1·28714	9·78	176·5	—	0	1·82631	1·72	176·8	104·0
Mixtures of Ether and 95·25(wt.)% H_2SO_4 at 30°.									
100	0·7021	0	2·134		35·911	1·26639	10·00	194·5	
79·076	0·84671	5·20	5·95		31·861	1·31474	9·73	200·1	
62·176	0·99339	9·44	23·01		26·966	1·37645	9·28	195·0	
54·578	1·06685	—	53·65		17·016	1·51579	7·84	169·1	
46·539	1·14855	10·06	120·1		9·002	1·64790	6·22	156·2	
42·351	1·19363	10·16	159·7		4·988	1·72182	5·27	157·0	
40·074	1·21850	10·07	173·3		0	1·82385	3·87	167·7	
Mixtures of Ether and 84·10(wt.)% H_2SO_4 at 30°.									
100	0·7021	0	2·134	0·00	34·918	1·23660	10·32	292·4	11·92
59·088	1·0041	9·00	62·6	3·67	28·580	1·30565	10·00	267·8	20·47
55·338	1·03965	9·75	—	—	18·753	1·43020	9·42	214·8	46·03
50·633	1·08563	—	129·1	5·255	10·040	1·56499	9·04	188·0	81·76
49·683	1·09258	10·37	—	—	4·417	1·66732	8·73	181·5	111·4
45·501	1·13316	10·58	205·1	6·000	1·750	—	—	—	126·8
40·192	1·18388	10·46	273·9	7·93	0	1·75946	8·56	179·8	142·3
Mixtures of Ether and 49·77(wt.)% H_2SO_4 at 30°.									
100	0·7021	0	2·134	0·000	10·428	1·28614	8·02	40·60	386·8
17·589	1·2260	8·53	46·1(?)	141(?)	4·415	1·34062	7·52	34·55	535·5
14·057	1·25373	8·82	44·58	317·0	2·257	1·36180	7·28	32·26	599·6
11·300	1·27758	8·00	41·77	367·1	0	1·38432	7·07	30·15	683·5

TABLE II.

Specific Conductivity (κ) of Mixtures of Ether and 95·0(wt.)% H_2SO_4 at 30°; "x" denotes the wt. percentage of ether.

x.	κ.	x.	κ.	x.	κ.	x.	κ.
100	0·000001	63·44	0·00236	37·80	0·01311	15·53	0·06994
80·77	0·00066	55·50	0·00340	36·485	0·01485	13·09	0·08047
76·35	0·00103	52·28	0·00393	36·235	0·01520	6·61	0·1122
74·99	0·00121	48·14	0·00480	31·96	0·02228	6·17	0·1143
71·90	0·00152	44·39	0·006854	24·10	0·03960	0	0·1374
63·68	0·00241	41·935	0·008724	20·70	0·04992		

TABLE III.

lixtures of Water and Sulphuric Acid at 30°.

ter. %.	$d_{4^\circ}^{30^\circ}$.	Contraction (c.c.).	Conductivity (κ).	Water. Wt. %.	$d_{4^\circ}^{30^\circ}$.	Contraction (c.c.).	Conductivity (κ).
00	0·9957	0·000	0·0000	25	1·6597	9·130	0·2053
95	1·0281	0·905	0·2388	20	1·7170	9·040	0·1568
90	1·0617	1·766	0·4520	15	1·7678	8·400	0·1410
85	1·0968	2·600	0·6320	12	1·7915	7·570	—
80	1·1335	3·404	0·7660	10	1·8038	6·705	0·1488
75	1·1718	4·175	0·8500	8	1·8136	5·858	0·1492
70	1·2115	4·822	0·8825	6	1·8210	4·760	—
65	1·2527	5·535	0·8720	5	1·8236	4·172	0·1369
60	1·2953	6·116	0·8260	4	1·8255	3·473	—
55	1·3400	6·664	0·7545	3	1·8264	2·740	0·1074
50	1·3872	7·202	0·6660	2	1·8261	1·932	—
45	1·4372	7·728	0·5680	1·58	—	—	0·0784
40	1·4898	8·216	0·4680	1·00	1·8242	1·020	—
35	1·5446	8·630	0·3708	0·92	—	—	0·04825
30	1·6014	8·948	0·2819	0	1·8205	0·000	0·0070

TABLE IV.

Viscosity (η) of Mixtures of Water and Sulphuric Acid at 30°; x " denotes the wt. percentage of Sulphuric Acid.

x.	η.	x.	η.	x.	η.	x.	η.
09·924	0·2134	88·733	0·1840	78·242	0·1350	58·356	0·0414
97·513	0·1724	86·865	0·1878	74·746	0·1077	49·858	0·02955
95·723	0·1674	85·070	0·1905	70·518	0·0805	43·234	0·02275
93·410	0·1691	82·580	0·1805	67·209	0·0649	26·492	0·01426
91·360	0·1752	80·243	0·1568	64·643	0·05625	15·699	0·01175
						0·000	0·0077

In conclusion, the author's thanks are due to several local gentlemen for indispensable help, to Selby & Co., of Melbourne, for providing ether and apparatus, to Mr. W. M. Holmes, of Melbourne University, for standardising the thermometers, and to Professor Masson for his kind interest in this paper.

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NOTE.—It is assumed above that mixtures of ether, sulphuric acid, and water are completely resolvable into their components. The densities of several such mixtures were found to alter slightly after keeping for several months at the ordinary temperature; hence the occurrence of chemical action between the components, such as formation of ethyl hydrogen sulphate, is probable, but this is so slow that the above assumption can be considered unaffected.

CVIII.—2-p-*Dimethylaminostyrylpyridine Methiodide, a New Photographic Sensitiser.*

By William Hobson Mills and William Jackson Pope.

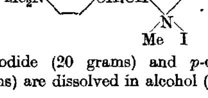
Several classes of basic dyestuffs have been described which are related in constitution to Greville Williams's cyanine and resemble it by possessing in an exceptional degree the property of acting as photographic sensitisers; all these substances contain the quinoline, or the closely related benzothiazole, nucleus. It was thus of interest to ascertain whether the presence of such a condensed nucleus is essential to the development of intense photosensitising action in dyes of these classes.

König stated (*J. pr. Chem.*, 1912, [ii], **86**, 172) that colouring matters apparently analogous to the cyanines could be obtained by condensing *p*-dimethylaminobenzaldehyde with quinaldinium and lepidinium salts with the aid of piperidine, but that these substances had not been more closely investigated. Barbier later studied this reaction (*Bull. Soc. chim.*, 1920, [iv], **27**, 427), and described the preparation and properties of various condensation products obtained by its means, and a large number of similar compounds have recently been described by König and Treichel (*J. pr. Chem.*, 1921, [ii], **102**, 63). Neither Barbier nor König suggests that any of the substances prepared by him, which contain quinoline or benzothiazole nuclei, exhibit properties which make them of special value as sensitisers.

We have found that a similar kind of condensation occurs between *p*-dimethylaminobenzaldehyde and 2-methylpyridine methiodide, yielding 2-p-*dimethylaminostyrylpyridine methiodide*, and that this substance proves to be the most powerful sensitiser for green light yet known for gelatino-silver bromide photographic plates. The new sensitiser is the simplest member of a novel series of compounds which may be expected to act as photographic sensitisers.

Experimental.

2-p-*Dimethylaminostyrylpyridine Methiodide,*



α-Picoline methiodide (20 grams) and *p*-dimethylaminobenzaldehyde (12·7 grams) are dissolved in alcohol (270 c.c.), piperidine

·5 c.c.) is added, and the solution boiled for five hours; the quid rapidly assumes a deep orange colour and, after cooling, eposits a red, crystalline substance. On recrystallisation from ıethyl alcohol, the compound is obtained in bright red prisms which show a blue reflex and melt at 275° (Found: C = 52·6; I = 5·2; I = 34·8. $C_{16}H_{19}N_2I$ requires C = 52·5; H = 5·2; I = 34·7 per cent.).

Aqueous solutions of the compound dye silk a bright orange-yellow colour which is not fast to light; they are decolorised by the addition of mineral acids, but less readily than are those of the *iso*cyanines. The orange-coloured alcoholic solutions show a band of selective absorption in the blue and green with obscurely marked maxima at about λ 4750 and λ 4600. Gelatino-bromide plates, after bathing in aqueous solutions containing one part of the dyestuff in thirty or forty thousand parts of solution and drying, show almost uniform sensitiveness to light of all wave-lengths from the blue to about λ 5600; the photosensitiveness then falls off rapidly until it ends at about λ 6200. It is note-worthy that the failure to sensitise gelatino-bromide plates for a short region in the bluish-green, which occurs so frequently with sensitisers for the yellow and red regions of the spectrum, does not occur with the substance now described.

A number of sensitising dyestuffs of this novel type may be prepared by replacing the α-picoline by its many easily obtainable derivatives.

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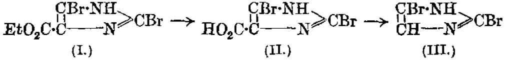
CIX.—*Bromo-derivatives of Glyoxaline.*

By ISIDORE ELKANAH BALABAN and FRANK LEE PYMAN.

THIS investigation was carried out with the object of preparing the mono- and di-bromoglyoxalines. The sole bromination product of glyoxaline hitherto described is the fully brominated substance, 2 : 4 : 5-tribromoglyoxaline (IV), which was prepared by Wyss (*Ber.*, 1877, **10**, 1365) by the action of bromine on glyoxaline in ethereal solution. Since one of us has shown (T., 1910, **97**, 1814) that the bromination of 4-methylglyoxaline with one molecular proportion of bromine in chloroform solution at − 10° to − 12° results in the formation of a monobromo-4-methylglyoxaline in a yield of 34 per cent. of the theoretical (together with 2 : 5-dibromo-

4-methylglyoxaline in a yield of 12 per cent. of the theoretical), similar conditions have been employed in brominating glyoxaline itself, but this resulted in the formation of 2 : 4 : 5-tribromoglyoxaline and glyoxaline hydrobromide together with a considerable quantity of ammonium bromide and only a trace of 4 : 5-dibromoglyoxaline. This difference in behaviour of glyoxaline and its 4-methyl homologue towards halogenating agents is reflected by Pauly's observation (*Ber.*, 1908, **41**, 3999) that *N*/10-iodine solution reacts with these bases in aqueous alkali to yield tri-iodoglyoxaline and monoiodo-4-methylglyoxaline (together with a small amount of a more highly iodated product), respectively.

In view of an observation by Pauly (*Ber.*, 1910, **43**, 2243) that tetraiodohistidine anhydride is converted into di-iodohistidine anhydride by the action of warm aqueous sodium sulphite, it seemed probable that the partial reduction of 2 : 4 : 5-tribromoglyoxaline might be effected similarly, and experiment has shown that when this compound is boiled with a limited quantity of sodium sulphite in 20 per cent. aqueous solution, it yields a monobromoglyoxaline together with small quantities of a dibromoglyoxaline, melting at 225°, a bromoglyoxalinesulphonic acid, and glyoxaline. In order to determine the orientation of these products, 2 : 5-dibromoglyoxaline was prepared. This was effected by brominating ethyl glyoxaline-4-carboxylate, when *ethyl* 2 : 5-*dibromoglyoxaline*-4-*carboxylate* (I) was obtained. On boiling this compound with hydrochloric acid, it suffered hydrolysis with the formation of 2 : 5-*dibromoglyoxaline*-4-*carboxylic acid* (II), which then underwent decarboxylation with the formation of 2 : 5-*dibromoglyoxaline* (III).

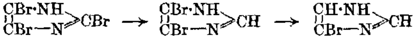


(I.) (II.) (III.)

This substance melts at 193° and is not identical with the dibromoglyoxaline resulting from the reduction of tribromoglyoxaline, which must consequently be 4 : 5-*dibromoglyoxaline* (V). It will be observed that the more symmetrical of the two dibromoglyoxalines possesses the higher melting point, as would be expected from previous knowledge of the relation between chemical constitution and fusibility, and it may be pointed out that the 4 : 5-substituted dimethyl- and diphenyl-glyoxalines also have higher melting points than the 2 : 5-isomerides.

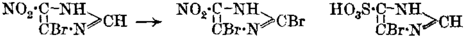
Orientation of the monobromoglyoxaline follows from the fact that it may be obtained by the partial reduction of 4 : 5-dibromoglyoxaline by means of sodium sulphite and is therefore 4-*bromo*-

glyoxaline (VI). The formation of this compound may consequently be represented by the following scheme :



(IV.) (V.) (VI.)

Nitration of 4-bromoglyoxaline leads to 4-*bromo*-5-*nitroglyoxaline* (VII), the position of the nitro-group being proved by the fact that the bromonitro-compound yields on bromination the same substance, which is obtained by the nitration of 2 : 5-dibromoglyoxaline, namely, 2 : 4-*dibromo*-5-*nitroglyoxaline* (VIII).



(VII.) (VIII.) (IX.)

Attempts to nitrate 4 : 5-dibromoglyoxaline were unsuccessful, like previous efforts to nitrate 4 : 5-dimethylglyoxaline (Fargher and Pyman, T., 1919, **115**, 219), and the results afford confirmatory evidence that the glyoxaline nucleus is incapable of nitration in the 2-position.

The bromoglyoxalinesulphonic acid resulting from the interaction of tribromoglyoxaline and sodium sulphite contains the bromine atom in the 4-position, for it yields 4-bromoglyoxaline on hydrolysis. It may also be prepared from 4-bromoglyoxaline by direct sulphonation, and is therefore almost certainly 4-*bromoglyoxaline*-5-*sulphonic acid* (IX), for there can be little doubt that the sulpho-group substitutes a hydrogen atom of the nucleus in the same position as does the nitro-group. An attempt to solve the problem directly by the action of sodium sulphite on the small quantities of 2 : 5- and 4 : 5-dibromoglyoxalines available gave 4-bromoglyoxaline as the only identifiable product in each case.

The investigation is being continued.

EXPERIMENTAL.

Bromination of Glyoxaline.

A solution of 120 grams of glyoxaline in 720 c.c. of chloroform was treated with 276 grams of bromine (1 mol.) in 360 c.c. of chloroform at the ordinary temperature. After removing the solvent, the residue was boiled with water, when 112 grams of tribromoglyoxaline, melting at 210—212°, remained undissolved. This was dissolved in cold aqueous sodium hydroxide and precipitated fractionally by hydrochloric acid, when 109 grams of tribromoglyoxaline melting at 220° were deposited, no evidence

of the presence of a dibromoglyoxaline being obtained. The mother-liquor was concentrated and deposited 20 grams of ammonium bromide. The filtrate from this gave a residue amounting to 165 grams and consisting mainly of crude glyoxaline hydrobromide. A third of this residue was neutralised with sodium carbonate, when it deposited 1 gram of very crude tribromoglyoxaline, and was extracted with ether. The extract (1·4 grams) was converted into the hydrochloride and gave 0·27 gram of 4 : 5-dibromoglyoxaline hydrochloride, which melted and decomposed at 250° (corr.), and was identified by conversion into the base, which melted at 225° (corr.) alone or mixed with 4 : 5-dibromoglyoxaline resulting from the reduction of tribromoglyoxaline. 2 : 4 : 5-Tribromoglyoxaline crystallises from glacial acetic acid in colourless, silky needles, which melt and decompose at 221° (corr.). [Wyss (*loc. cit.*) gives m. p. 214°.] It is soluble in about 280 parts of boiling water (Found: Br = 79·1. Calc., Br = 78·7 per cent.).

Action of Sodium Sulphite on Tribromoglyoxaline.

1. Ninety grams of tribromoglyoxaline were boiled with a solution of 180 grams of hydrated sodium sulphite (approx. 2·3 mols.) in 20 per cent. aqueous solution for three hours under reflux and kept, when 19·1 grams of crystals melting at 140—160° were deposited (mother-liquor M). The crystals were dissolved in cold aqueous sodium hydroxide and precipitated fractionally by hydrochloric acid, when 4 : 5-dibromoglyoxaline was precipitated first, followed by unchanged tribromoglyoxaline. The former was refractionated in the same way and finally crystallised from glacial acetic acid, when 3·5 grams of the pure compound were obtained.

The mother-liquor (M) was mixed with excess of strong hydrochloric acid, evaporated to low bulk, and extracted with alcohol, when inorganic salts were removed. The extract was deprived of the solvent, and made alkaline with sodium carbonate, when crude 4-bromoglyoxaline was in part precipitated and in part collected by extraction with ether (aqueous mother-liquor N). The crude base was converted into the picrate and crystallised several times from water, when 53·0 grams of pure 4-bromoglyoxaline picrate were obtained, that is, 47·8 per cent. of the theoretical yield. The final mother-liquors from the crystallisation of the picrates gave 1·6 grams of glyoxaline picrate, which melted at 212° (corr.) alone or mixed with a specimen prepared from glyoxaline.

The aqueous mother-liquor (N) was acidified with hydrochloric acid, evaporated nearly to dryness, and extracted with alcohol. On removing the solvent, there remained about 20 grams of a viscid, brown syrup, which was dissolved in a little water and

kept, when crystals were deposited. After several crystallisations from water, these gave 3·0 grams of pure bromoglyoxalinesulphonic acid, whilst the mother-liquors contained other crystalline compounds, which have not yet been isolated in a pure state.

2. On boiling 30 grams of *tribromoglyoxaline* with sodium sulphite (5 mols.) in 20 per cent. aqueous solution for eight hours, no crystals were deposited on cooling, and 21·3 grams of 4-bromoglyoxaline picrate were obtained, that is, 57·6 per cent. of the theoretical yield.

4-*Bromoglyoxaline*.

4-*Bromoglyoxaline* crystallises from water in colourless, elongated plates, and from chloroform or benzene in glistening plates which melt at 130—131° (corr.). It is easily soluble in hot, somewhat sparingly soluble in cold, water, giving a solution neutral to litmus. It is easily soluble in alcohol, ether, acetone, or ethyl acetate, sparingly soluble in cold chloroform or benzene, and very sparingly soluble in light petroleum. It is readily soluble in dilute mineral acids, ammonia, or sodium hydroxide, but not in sodium carbonate (Found: C = 24·3, 24·3; H = 2·2, 2·1; N = 19·2, 19·4; Br = 54·7, 54·5. $C_3H_3N_2Br$ requires C = 24·5; H = 2·0; N = 19·1; Br = 54·4 per cent.).

The *hydrochloride* crystallises from 5*N*-hydrochloric acid in colourless, elongated prisms, which, when air-dried, contain a variable amount of water of crystallisation, and after drying at 100°, melt at 162—165° (corr.). It is very easily soluble in water, giving a strongly acid solution (Found: in air-dried salt, loss at 100° = 4·8, 5·9; 7·5, 8·0. $C_3H_3N_2Br,HCl,H_2O$ requires H_2O = 8·9 per cent. Found: in salt dried at 100°, Cl = 19·0. $C_3H_3N_2Br,HCl$ requires Cl = 19·3 per cent.).

The *nitrate* crystallises from water in stout needles, which are anhydrous and melt and decompose at 135° (corr.). It is soluble in about 5 parts of boiling water, and somewhat sparingly soluble in cold water (Found: N = 20·4. $C_3H_3N_2Br,HNO_3$ requires N = 20·0 per cent.).

The *hydrogen oxalate* crystallises from water in slender, glistening needles, which are anhydrous and melt and decompose at 218° (corr.) after previous sintering. It is soluble in about 4·5 parts of boiling water, and sparingly soluble in cold water (Found: C = 25·3, 25·2; H = 2·1, 2·4. $C_3H_3N_2Br,C_2H_2O_4$ requires C = 25·3; H = 2·1 per cent.).

The *picrate* crystallises from water in stout, yellow needles which melt at 162° (corr.), and are anhydrous. It is soluble in about 14 parts of boiling water, but is very sparingly soluble

cold water (Found : N = 18·3, 18·5. $C_3H_3N_2Br,C_6H_3O_7N_3$ requires N = 18·6 per cent.).

Nitration of 4-Bromoglyoxaline.—6·45 Grams of 4-bromoglyoxaline nitrate were added to 35 c.c. of concentrated sulphuric acid with constant cooling with water. After heating for one hour on the water-bath, the product was diluted with ice-water, when it deposited 5·12 grams of the pure nitro-compound, that is, 87 per cent. of the theoretical yield.

4-*Bromo-5-nitroglyoxaline* crystallises from water in stout, colourless needles which melt and decompose at 279° (corr.) after previous sintering (Found : C = 18·5; H = 1·5; N = 21·7, 21·8; Br = 41·7, 41·8. $C_3H_2O_2N_3Br$ requires C = 18·7; H = 1·0; N = 21·9; Br = 41·7 per cent.). It is soluble in about 250 parts of boiling water, and almost insoluble in cold water. It is sparingly soluble in hot alcohol, and very sparingly soluble in ether, chloroform, or cold alcohol. It is insoluble in 5*N*-hydrochloric acid, but dissolves in concentrated hydrochloric acid, giving a colourless solution, from which it is precipitated on dilution with water. It dissolves in aqueous sodium hydroxide, sodium carbonate, or ammonia, giving yellow solutions.

Bromination of 4-Bromo-5-nitroglyoxaline.—0·5 Gram of 4-bromo-5-nitroglyoxaline was dissolved in 6·5 c.c. of water containing 0·3 gram of sodium hydroxide, and bromine was added drop by drop, with shaking and cooling with water, until the solution was acid. The yellow precipitate was collected and crystallised from water, when 0·3 gram of 2 : 4-dibromo-5-nitroglyoxaline separated in flat needles, which darkened from about 170° alone or mixed with the product of nitration of 2 : 5-dibromoglyoxaline (p. 958), with which it agreed in its properties (Found : N = 15·7; Br = 59·1. $C_3HO_2N_3Br_2$ requires N = 15·5; Br = 59·0 per cent.).

Sulphonation of 4-Bromoglyoxaline.—Two grams of 4-bromoglyoxaline were converted into the sulphate by the addition of 1 c.c. of sulphuric acid, 6·6 c.c. of 70 per cent. oleum were added and the mixture was heated for three hours in an oil-bath at 160°. The product was diluted with water, sulphuric acid removed by barium hydroxide, and excess of the latter by carbon dioxide, when 3·92 grams of barium bromoglyoxalinesulphonate were obtained. This was dissolved in water, freed from barium by means of sulphuric acid, and concentrated, when 2·85 grams of bromoglyoxalinesulphonic acid were obtained, that is, 85 per cent. of the theoretical yield. It melted and decomposed at 280° (corr.) alone or mixed with the bromoglyoxalinesulphonic acid resulting from the interaction of tribromoglyoxaline and sodium sulphite, described on p. 954, with which it agreed in its properties

(Found: in air-dried substance, loss at 120° = 7·4; Br = 32·7. $C_3H_3O_3N_2BrS,H_2O$ requires H_2O = 7·3; Br = 32·6 per cent.).

4 : 5-*Dibromoglyoxaline.*

4 : 5-*Dibromoglyoxaline* crystallises from water in fine, colourless needles and from glacial acetic acid in short, stout needles, which melt at 225° (corr.) (Found: C = 15·7, 15·8; H = 1·4, 1·1; N = 12·5, 12·1; Br = 71·2, 70·9. $C_3H_2N_2Br_2$ requires C = 15·9; H = 0·9; N = 12·4; Br = 70·8 per cent.).

It is sparingly soluble in hot, very sparingly soluble in cold, water, giving a solution neutral to litmus, easily soluble in alcohol, ether, acetone, ethyl acetate, or glacial acetic acid, but very sparingly soluble in chloroform, benzene, or light petroleum. It is soluble in cold aqueous sodium hydroxide or carbonate or in ammonia. It is insoluble in cold 5*N*-hydrochloric acid, forming the sparingly soluble *hydrochloride,* which dissolves on heating the solution, and crystallises on cooling in glistening plates which effervesce and decompose at 250° (corr.). This salt remains unchanged after heating at 100°, but dissociates on the addition of water, giving the base, melting at 225°. The *nitrate* crystallises from dilute nitric acid in elongated plates, which melt and decompose at about 115° (corr.).

Reduction of 4 : 5-*Dibromoglyoxaline by Sodium Sulphite.*—(*a*) Three grams of 4 : 5-dibromoglyoxaline were boiled under reflux with a solution of 3·4 grams of hydrated sodium sulphite (1 mol.) in 17 c.c. of water for five hours, and the solution was filtered hot from 1·45 grams of unchanged material, melting at 225°, kept, filtered from 0·25 gram, melting at 220°, basified with sodium carbonate, and extracted with ether, when 0·7 gram of crude 4-bromoglyoxaline, melting at 100—110°, was collected. This gave 1·5 grams of the pure picrate, melting at 162° (corr.). The yield thus amounts to 30 per cent. of the theoretical. To confirm the identity of the product, the picrate was converted through the hydrochloride into the base, which melted at 130—131° (corr.) alone or mixed with 4-bromoglyoxaline resulting from the reduction of 2 : 4 : 5-tribromoglyoxaline.

(*b*) Three grams of 4 : 5-dibromoglyoxaline were boiled with a solution of 10·0 grams of hydrated sodium sulphite (3 mols.) for six hours, and the solution was basified with sodium carbonate and extracted with ether, when 1·8 grams of crude 4-bromoglyoxaline, melting at 125—127°, were obtained, which gave 4·05 grams of the pure picrate melting at 162° (corr.), that is, 80 per cent. of the theoretical yield.

Attempted Nitration of 4 : 5-*Dibromoglyoxaline.*—To 0·5 gram of

4 : 5-dibromoglyoxaline there was added 0·5 c.c. of concentrated nitric acid followed by 1·0 c.c. of concentrated sulphuric acid, the mixture being cooled meanwhile with ice-water. After keeping for fifteen minutes, when slight evolution of bromine was observed, the solution was divided into two parts. The first was diluted with a little water, when 4 : 5-dibromoglyoxaline nitrate separated, and gave the base melting at 225° on crystallisation from water. The second was heated for a few minutes on the water-bath, when a vigorous evolution of bromine took place, and then diluted with water, when a clear solution was obtained. Neither this solution nor the crystals or filtrate from the first portion gave any yellow colour with sodium hydroxide.

4-*Bromoglyoxaline*-5-*sulphonic Acid.*

4-*Bromoglyoxaline*-5-*sulphonic acid* crystallises from water in glistening prisms, which contain $1H_2O$ and after drying at 120° melt and decompose at 280° (corr.). It is soluble in less than 2 parts of boiling water and in about 35 parts of cold water, and almost insoluble in absolute alcohol (Found : in air-dried substance, loss at 120° = 7·4, 7·4. $C_3H_3O_3N_2BrS,H_2O$ requires H_2O = 7·3 per cent. Found : in substance dried at 120°, C = 15·9, 15·4 ; H = 1·3, 1·7 ; N = 12·3, 12·4 ; Br = 35·6 ; S = 14·3. $C_3H_3O_3N_2BrS$ requires C = 15·9 ; H = 1·3 ; N = 12·3 ; Br = 35·3 ; S = 14·1 per cent.).

The *barium* salt crystallises from water in flat needles which are anhydrous and easily soluble in water, giving a solution neutral to litmus [Found : Ba = 23·0, 23·2. $(C_3H_2O_3N_2BrS)_2Ba$ requires Ba = 23·3 per cent.].

Hydrolysis of the Sulphonic Acid.—0·5 Gram was heated with 5 c.c. of concentrated hydrochloric acid for three hours at 170°. The clear, colourless solution was evaporated to a syrup, and mixed with aqueous sodium carbonate, when 0·15 gram of crude 4-bromoglyoxaline separated; this, after recrystallisation from water, melted at 130—131° (corr.) alone or mixed with a specimen prepared by the reduction of tribromoglyoxaline.

Glyoxaline-4-*carboxylic Acid.*

Fargher and Pyman (T., 1919, **115**, 228) have shown that this acid may be prepared from glyoxaline-4 : 5-dicarboxylic acid by way of glyoxaline-4-carboxyanilide. Considerable quantities of the acid were required for conversion into the ethyl ester, and the methods previously described have been improved.

In the preparation of the anilide, the "residual aqueous solution" from the steam distillation (*loc. cit.*, p. 229, l. 3) is acidified

with hydrochloric acid, filtered from unchanged dicarboxylic acid, and basified with sodium carbonate, when the anilide crystallises out contaminated with a sticky resin, which is readily removed by washing the product with ether, leaving the anilide in a nearly pure state, melting at about 224°. The yield is about 50 per cent. of the theoretical, whilst glyoxaline can be recovered from the mother-liquors in a yield of about 10 per cent. of the theoretical. The loss is mainly due to the decomposition of the glyoxaline nucleus with the formation of ammonia, for, on boiling the dicarboxylic acid with aniline, ammonium carbonate is deposited in the condenser in a yield amounting to 33 per cent. of the theoretical.

The hydrolysis of the anilide is readily effected by boiling its solution in concentrated hydrochloric acid (5 parts) for four hours under reflux. The product is worked up as described previously, except that the aniline is removed by distillation with steam, and gives glyoxaline-4-carboxylic acid in a yield of 75 per cent. of the theoretical, the loss being due mainly to the formation of ammonia by the disruption of the glyoxaline nucleus.

Bromination of Ethyl Glyoxaline-4-carboxylate. Formation of Ethyl 2 : 5-Dibromoglyoxaline-4-carboxylate.

To 22 grams of ethyl glyoxaline-4-carboxylate (T., 1916, **109**, 200) partly dissolved in 100 c.c. of chloroform, a solution of 15 c.c. of bromine in 100 c.c. of chloroform was added at 15—20°. The product was mixed with 50 c.c. of water and the solvent and excess of bromine were removed by a current of steam. The residue was cooled and filtered from crude ethyl 2 : 5-dibromoglyoxaline-4-carboxylate, which, after recrystallisation from 2·5 litres of water, gave 19·0 grams of the pure substance. The mother-liquors were basified with sodium carbonate, and extracted with chloroform, when 10·2 grams of crude ethyl glyoxaline-4-carboxylate were recovered. On brominating this under the same conditions, another 7·1 grams of the pure dibromo-ester were obtained, whilst 3·7 grams of crude ethyl glyoxaline-4-carboxylate were recovered. The total yield of dibromo-ester, 26·1 grams, amounts to 56 per cent. of the theoretical.

Ethyl 2 : 5-dibromoglyoxaline-4-carboxylate crystallises from water in stout, prismatic needles which are anhydrous and melt at 147° (corr.) (Found: C = 23·9, 24·0; H = 2·3, 1·9; N = 9·6, 9·5; Br = 54·0. $C_6H_6O_2N_2Br_2$ requires C = 24·2; H = 2·0; N = 9·4; Br = 53·7 per cent.).

It dissolves in rather more than 100 parts of boiling water, and the greater part crystallises from the solution on cooling. It is very easily soluble in alcohol, ether, acetone, or ethyl acetate;

easily soluble in glacial acetic acid or chloroform; sparingly soluble in benzene, and almost insoluble in light petroleum. It dissolves in 5*N*-hydrochloric acid, but is precipitated on dilution with water. It is readily soluble in cold aqueous solutions of sodium hydroxide, sodium carbonate, or ammonia.

Hydrolysis of Ethyl 2 : 5-Dibromoglyoxaline-4-carboxylate.—Hydrolysis of the dibromo-ester leads to the dibromo-acid and 2 : 5-dibromoglyoxaline, the nature of the product depending on the time of heating and the concentration of the acid. The dibromo-acid has not been isolated in good yield, for conditions sufficiently vigorous to ensure the complete hydrolysis of the ester also effect a measure of decarboxylation.

(1) *Formation of 2 : 5-Dibromoglyoxaline-4-carboxylic Acid.*—Ten grams of the dibromo-ester were boiled with 50 c.c. of concentrated hydrochloric acid and 75 c.c. of water for one hour under reflux and the solution was evaporated to dryness on a water-bath. The residue was dissolved in 20 c.c. of water and kept, when 0·9 gram of the dibromo-acid was deposited. The mother-liquor was mixed with aqueous sodium carbonate until only faintly alkaline to methyl-orange and kept, when 1·9 grams of crude dibromo-ester were collected. On concentrating the filtrate and adding hydrochloric acid, 3·0 grams of the dibromo-acid separated in a nearly pure state, and further quantities were obtained by evaporating the mother-liquors to dryness, separating sodium chloride by means of alcohol, and crystallising the residue of the alcoholic extract from water. The crude acid was purified by recrystallisation from ten times its weight of water, and 4·2 grams of the acid were isolated in a pure state, that is, 38 per cent. of the theoretical.

2 : 5-*Dibromoglyoxaline*-4-*carboxylic acid* crystallises from water in glistening, prismatic needles containing $3H_2O$, or in quadrilateral plates containing $\frac{1}{2}H_2O$. After drying at 100°, it effervesces and turns brown at 225° (corr.) (Found: in air-dried needles, H_2O = 15·6, 15·6. $C_4H_2O_2N_2Br_2,3H_2O$ requires H_2O = 16·7 per cent. Found: in air-dried plates, H_2O = 3·3, 3·3. $C_4H_2O_2N_2Br_2,\frac{1}{2}H_2O$ requires H_2O = 3·3 per cent. Found: in substance dried at 100°, C = 17·6; H = 1·2; N = 10·1; Br = 59·5. $C_4H_2O_2N_2Br_2$ requires C = 17·8; H = 0·7; N = 10·4; Br = 59·3 per cent.).

The acid is easily soluble in hot water, sparingly soluble in cold, very easily soluble in alcohol, ether, ethyl acetate, or acetone, and almost insoluble in chloroform, benzene, or light petroleum. It is soluble in 5*N*-hydrochloric acid and in cold aqueous sodium hydroxide, sodium carbonate, or ammonia.

(2) *Formation of 2 : 5-Dibromoglyoxaline.*—Twelve grams of the dibromo-ester were boiled with 120 c.c. of concentrated hydrochloric

acid and 60 c.c. of water for eight hours under reflux. The liquor was evaporated to dryness and the residue moistened with water and evaporated to dryness several times. The residue was digested with water and kept, when 4·2 grams of 2 : 5-dibromoglyoxaline, melting at 192°, separated. The mother-liquor, on evaporation to dryness and treatment with water, gave another 2·1 grams of the same compound, equally pure, and, after the addition of sodium carbonate until the solution was only faintly acid to methyl-orange, deposited 0·8 gram, melting at 190°. The total yield, 7·1 grams, amounts to 78 per cent. of the theoretical.

2 : 5-*Dibromoglyoxaline.*

2 : 5-*Dibromoglyoxaline* crystallises from water in prismatic needles, which are anhydrous and melt to a clear, colourless liquid at 193° (corr.) (Found : C = 15·8, 15·7; H = 1·2, 1·2; N = 12·8, 12·7; Br = 70·8, 70·7. $C_3H_2N_2Br_2$ requires C = 15·9; H = 0·9; N = 12·4; Br = 70·8 per cent.). It is soluble in about 100 parts of boiling water, but very sparingly soluble in cold water, giving a solution neutral to litmus. It is very easily soluble in alcohol, acetone, or ethyl acetate, easily soluble in ether or glacial acetic acid, but very sparingly soluble in chloroform, benzene, or light petroleum. It is soluble in 5*N*-hydrochloric acid, and is not precipitated on dilution. It dissolves in aqueous sodium hydroxide or carbonate, and in aqueous ammonia.

The *hydrochloride* crystallises from concentrated hydrochloric acid in prisms, which, after air-drying, sinter from about 100° and melt between 120° and 130°. When the salt is dried at 100°, the base, melting at 193°, remains, the decrease in weight (20·5 per cent.) approximating to that required (19·4 per cent.) for the loss of the HCl plus H_2O from $C_3H_2N_2Br_2,HCl,H_2O$. It is readily soluble in cold, very readily soluble in hot, concentrated hydrochloric acid. It dissociates on the addition of water, yielding a precipitate of the base.

Reduction of 2 : 5-*Dibromoglyoxaline by Sodium Sulphite.*—Nine grams of 2 : 5-dibromoglyoxaline were boiled under reflux with a solution of 10·2 grams of hydrated sodium sulphite (1 mol.) in 50 c.c. of water for four hours. After cooling, the liquor was filtered, and the crude unchanged dibromo-compound was dissolved in dilute hydrochloric acid and precipitated by the addition of sodium carbonate, when 2·5 grams, melting at 190°, were recovered. The combined filtrates were basified with sodium carbonate and extracted with ether, which removed 3·5 grams of crude 4-bromoglyoxaline. The aqueous mother-liquor was acidified with hydrochloric acid, and evaporated to dryness. The residue was extracted with alcohol, which removed a very small quantity

of brown syrup, which crystallised on the addition of water. The crystals, which were obtained in quantity only sufficient for the determination of melting point, softened at 160° and effervesced and decomposed at 240°, whilst 4-bromoglyoxaline-5-sulphonic acid decomposed at 270°, and a mixture of the two substances at 230°, in the same bath.

The crude 4-bromoglyoxaline was purified by conversion into the picrate and crystallisation from water, when 7·75 grams of the pure salt, melting at 162° (corr.), were obtained. The yield thus amounts to 51 per cent. of the theoretical calculated on the 9·0 grams employed, or 74 per cent. of the theoretical allowing for the 2·5 grams of recovered dibromo-compound. To confirm the identity of the product, the picrate was converted through the hydrochloride into the base, which melted at 130—131° (corr.) alone or mixed with 4-bromoglyoxaline resulting from the reduction of 2 : 4 : 5-tribromoglyoxaline.

Nitration of 2 : 5-Dibromoglyoxaline.—One gram of 2 : 5-dibromoglyoxaline was mixed with 1 c.c. of concentrated nitric acid, and the paste added to 2 c.c. of concentrated sulphuric acid. After heating for a few minutes on the water-bath, a slight evolution of bromine was observed and the product was poured into ice-water, when 0·5 gram of the nitro-compound separated in a pure state.

2 : 4-*Dibromo-5-nitroglyoxaline* separates from water in flat needles, which blacken from about 170° and appear to be completely charred at 180°, but do not melt even at 270° (Found : N = 15·6; Br = 59·0. $C_3HO_2N_3Br_2$ requires N = 15·5; Br = 59·0 per cent.). It is sparingly soluble in hot, very sparingly soluble in cold, water. It is insoluble in concentrated hydrochloric acid, but dissolves in cold aqueous sodium hydroxide or carbonate, or in ammonia, giving pale yellow solutions.

*Behaviour of the Bromoglyoxalines towards Sodium Diazobenzene-*p-*sulphonate.*

Solutions of the substances described above in aqueous sodium carbonate gave the following results with sodium diazobenzene-*p*-sulphonate :—

4-Bromoglyoxaline	intense cherry-red solution.
4 : 5-Dibromoglyoxaline	pale cherry-red solution.
2 : 5-Dibromoglyoxaline	very pale orange solution.
2 : 5-Dibromoglyoxaline-4-carboxylic acid	very pale orange solution.
Ethyl 2 : 5-dibromoglyoxaline-4-carboxylate	negative.
4-Bromo-5-nitroglyoxaline	negative.
2 : 4-Dibromo-5-nitroglyoxaline	negative.
4-Bromoglyoxaline-5-sulphonic acid	orange solution, gradually deepening in colour.

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CX.—*The Properties of Ammonium Nitrate. Part II. Ammonium Nitrate and Water.*

By Ida L. Millican, Alfred Francis Joseph, and Thomas Martin Lowry.

In the preceding paper of this series it was shown that the freezing point of ammonium nitrate can be raised by careful purification and drying to 169·6°. The freezing point is, however, extremely sensitive to the influence of traces of moisture, and it appeared desirable, therefore, to make quantitative experiments to determine the magnitude of this effect. In view, moreover, of the fact that the freezing point of the salt lies within the range of easy experimental observation, a unique opportunity presented itself of plotting a complete equilibrium diagram for a soluble salt and water, a diagram which, in this instance, has the special interest of including four transition temperatures.

Previous determinations of the solubility of ammonium nitrate between 0° and 100° have been made by Schwarz (Preisschrift, Göttingen, 1892, p. 42), and between 12° and 40° by Müller and Kaufmann (*Z. physikal. Chem.*, 1903, **42**, 499). On the aqueous side of the diagram, measurements of the freezing point of solutions of the salt have been made by de Coppet (*Ann. Chim. phys.*, 1872, [iv], **25**, 544), who has also located the eutectic point at − 17·35° and 41·2 per cent. $NH_4 \cdot NO_3$ (*Z. physikal. Chem.*, 1897, **22**, 240).

Experimental.

First Series of Measurements: 90° *to* 170°.

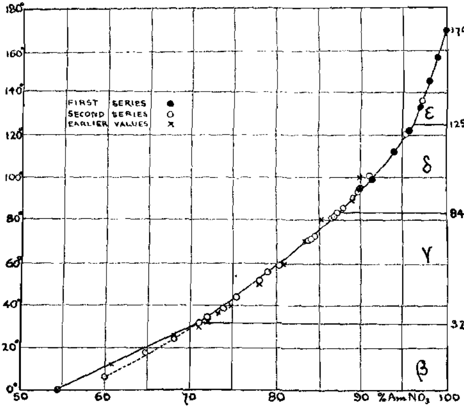
In the first series of measurements, the observations were made with mixtures of ammonium nitrate and water enclosed in sealed tubes, in order to avoid loss of the small quantities of water, which ranged only from 0 to 10 per cent. of the weight of ammonium nitrate. The tubes were suspended in a large beaker of liquid paraffin heated on a sand-bath. The liquid was stirred and its temperature read by means of a long standard thermometer. The temperature was noted at which most of the nitrate had melted, and then that at which the last traces were just disappearing; the mean of these two temperatures was taken as the temperature of dissolution. The bath was then allowed to cool until crystals reappeared; this point was recorded as the temperature of crystallisation. The mean of the temperatures of dissolution and crystallisation in a series of observations was taken as the initial freezing

point of the mixture. A correction for the exposed stem of the thermometer was made after the mean value of the initial freezing point had been determined. The method does not give results of a very high order of accuracy, but it is believed that the data are correct within 1°.

The numerical results are set out in Table I, and may be summarised as follows :

Water	0	1·05	2·01	3·20	4·39	6·24	8·76	10·04%
Freezing point	169	157	146	133	122	112	99	95°
Change of freezing point for 1 per cent. of water		11·4	11·4	10·9	—	5·4	5·2°	—

FIG. 1.



Equilibrium diagram for ammonium nitrate and water.

It will be seen that there is a very abrupt change in the magnitude of the effect produced by the addition of 1 per cent. of water, which at first lowers the freezing point by 11°, but afterwards only by about 5°. When plotted out as in Fig. 1, the two curves (one of which appears to be accurately rectilinear) intersect accurately at the transition temperature of 125°.

TABLE I.

Initial Freezing Point of Mixtures of Ammonium Nitrate and Water (First Series).

Water. Per cent.	Temperature of dissolution.	Temperature of crystallisation.	Initial freezing point.	Mean. Uncorrected.	Mean. Corrected.
4·39	122·6°	119°	120·8°	120°	122°
	120·8	118·6	119·7		
	120·4	118·6	119·5		
3·20	131·5	129·5	130·5	131	133
	132·5	130	131·2		
2·01	143	143	143	143	146
	142·5	141·5	142		
	144·5	143·5	144		
1·05	157·0	152·0	154·5	154	157
	154·6	152·0	153·3		
	155·2	153·4	153·3		
0*	166·2	163·4	164·8	165	169
	166·8	162·6	164·7		
6·24	110·4	106·4	108·4	110	112
	113·0	108·0	110·5		
	113·6	109·6	111·6		
0†	167·5	165·7	166·6	166	170
	167·8	165·0	166·4		
10·04	95·5	93·2	94·3	94	95
	95·5	93·0	94·2		
8·76	99·6	96·0	97·8	98	99
	97·6	96·8	97·2		
	101·3	96·4	98·8		

* Dried over sulphuric acid. † Dried over phosphoric oxide.

Second Series of Measurements: 6° to 136°.

In the second series of experiments, the initial freezing point of mixtures of ammonium nitrate and water was determined in a similar manner to that used for measuring the molecular depression of the freezing point in the Beckmann apparatus. The apparatus consisted of a tube 6 inches by 1 inch fitted with a rubber stopper carrying two thermometers and a stirrer; the stirrer fitted tightly in the rubber stopper and was lubricated by glycerol. The tube was immersed in a well-stirred bath of water or oil, the temperature of which was read to 0·1° by means of a standard thermometer; auxiliary thermometers for reading the temperature of the exposed thread of mercury were provided hoth inside and outside the tube. The ammonium nitrate was recrystallised three times, and dried during three or four days, until it no longer caked when allowed to cool in a stoppered bottle. About 20 grams were introduced into the tube, which was then corked and weighed; distilled water was added and the tube again weighed after its temperature had risen to that of the room. The rubber stopper with the thermometers and stirrer was then inserted and the tube immersed in a

bath, which was heated to a temperature about 5° above the melting point of the mixture, and then allowed to cool slowly while the mixture was stirred. The maximum temperature reached after crystallisation had started was recorded and the average taken of a series of concordant readings. It was found that a small quantity of water distilled off from the mixture and condensed on the side of the tube. An attempt was made to stop this by providing an additional stopper fitting like a piston immediately above the mixture, but this was not satisfactory. The moisture was therefore collected, with suitable precautions, on a weighed filter-paper, and a correction made for the water lost by the mixture, usually about 0·05 gram. A fresh mixture was made for each determination of the freezing point. The results obtained are recorded in Table II.

TABLE II.

Initial Freezing Point of Mixtures of Ammonium Nitrate and Water (Second Series).

Per cent. of ammonium nitrate in final mixture.	Initial freezing point. (Uncorrected.)	Corrected.	Per cent. of ammonium nitrate in final mixture.	Initial freezing point. (Uncorrected.)	Corrected.
59·70	6·6°	6·2°	84·43	72·2°	72·4°
64·64	17·2	16·9	86·56	81·2	81·4
68·03	24·8	24·5	86·84	81·2	81·7
71·05	32·15	31·9	87·11	83·2	83·8
71·84	34·4	34·3	87·84	85·2	85·6
73·80	38·2	38·1	88·99	89·6	90·4
75·71	43·8	43·7	89·70	92·8	93·7
78·04	51·5	51·5	91·10	99·2	100·1
78·85	55·2	55·3	91·09	100·0	100·9
80·24	58·3	58·4	95·23	119·6	120·8
83·77	70·8	71·0	97·14	134·1	135·8
83·96	71·3	71·4			

The second series of measurements extends over a range of temperatures which includes three transition points. The break at 125°, recorded in the first series of measurements, is accurately reproduced in the second series by drawing a straight line through the freezing point of the dry salt at 170° and the experimental observation at 136°. There is, however, no sign of a break at 84°, although it is unlikely that either the γ- or δ-form of the salt should be suppressed in such a long series of measurements; it would therefore appear that the solubilities of the γ- and δ-forms of the salt are not only identical at 84° but exhibit practically the same temperature coefficient at this temperature. The curve is, however, remarkable in that it also passes without a break through the transition temperature at 32°. In this case there is clear evidence that the freezing points are those of γ-ammonium nitrate,

persisting in a metastable form at temperatures below the normal transition point, since in these lower ranges of temperatures several determinations of the solubility of the salt are available, and a single measurement which we made of the composition of a solution saturated at the melting point of ice agrees closely with the value, 54 per cent. of $NH_4{\cdot}NO_3$, given by Müller and Kaufmann, whereas our main freezing-point curve would intersect the line of zero temperature at a point corresponding with 57 per cent. of $NH_4{\cdot}NO_3$.

The remainder of the equilibrium diagram can be plotted from data already available, so as to give a set of curves covering the whole range from 0 to 100 per cent. of ammonium nitrate. The eutectic temperature at $-17°$ is, however, so close to the transition temperature at $-16°$ that it is quite likely that this eutectic is for the common rhombic form of the salt rather than for the low-temperature tetragonal form.

Summary.

1. The influence of water on the freezing point of ammonium nitrate has been determined from 170° to 0°. It is therefore possible, with the help of earlier data, to plot a complete equilibrium diagram for ammonium nitrate and water.

2. The freezing-point curve shows a strongly-marked break at 125° and a small break at 32°, but appears to pass smoothly through the transition point at 84°.

3. Measurements have been made down to 6° of the solubility of the γ-form of the salt, which is only stable between 32° and 84°.

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CXI.—*The Properties of Ammonium Nitrate. Part III. Ammonium Nitrate and Sodium Nitrate.*

By REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY.

AMONGST the saline impurities commonly found in commercial ammonium nitrate, the most important is sodium nitrate, left behind by the incomplete conversion of the sodium salt into the ammonium salt in the process of manufacture. In the course of the experiments on the freezing point of ammonium nitrate (T., 1919, **115**, 1381), a few samples of commercial ammonium nitrate, in which the saline impurity was almost entirely confined to sodium nitrate, came under examination, and their freezing points were determined in the same way as for the pure salt, with the following results.

	Sodium nitrate present.	Freezing point (after drying).	Depression of freezing point.	Depression by 1 per cent. of $NaNO_3$.
Sample 1	8·8 per cent.	145·5°	24·1°	2·7°
„ 2	4·0 „ „	155·5	14·1	3·5
„ 3	1·7 „ „	164·0	5·6	3·3

These three samples show a depression of about 3° for every 1 per cent. of sodium nitrate, but the values are probably too high on account of the presence of small quantities of ammonium chloride, of which, for example, sample No. 3 contained 0·16 per cent. In order to secure exact information as to the influence of pure sodium nitrate on pure ammonium nitrate, an equilibrium diagram was plotted from 0 to 40 per cent. of sodium nitrate, and this diagram has been compared with that of silver nitrate and ammonium nitrate, for which data have been given by Zawidski (*Z. physikal. Chem.*, 1904, **47**, 721). These diagrams are of interest on account of the relationships which are involved between the various forms of the polymorphous nitrates.

EXPERIMENTAL.

Freezing Points of Mixtures of Pure Ammonium and Sodium Nitrates.

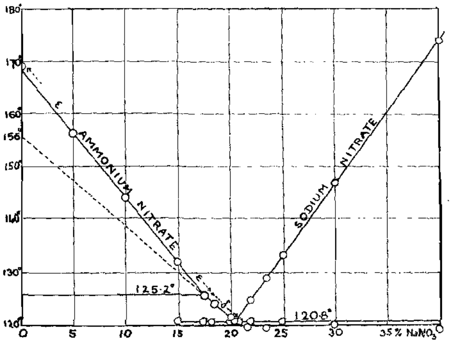
In the present series of experiments the freezing points of mixtures of ammonium and sodium nitrates, containing up to 40 per cent. of the latter salt, were determined. The apparatus was similar to that described in Part I for the determination of the freezing point of ammonium nitrate, except that the outer hot-water jacket was dispensed with, the air-jacket between the large and small boiling-tubes serving to prevent the over-rapid cooling of the contents of the smaller tube. This arrangement had the advantage that the fine crystals first appearing in the "melt" could be detected much more readily than when an outer bath of liquid was used.

The method of experiment was as follows. Ammonium nitrate was weighed into the inner boiling-tube, and the exact quantity of sodium nitrate corresponding with a mixture of the required composition was weighed on a piece of glazed paper, the weight of the two salts being about 20 grams in each experiment. The ammonium nitrate was melted over a small flame with constant stirring, and when completely molten the sodium nitrate was added slowly, and dissolved by continuous stirring and gentle heating. The tube and stirrer were clamped within the larger tube, a standard thermometer (graduated from 0° to 200° in fifths) inserted, and the space between the two tubes closed at the top with cotton-wool. The "melt" was stirred and the temperature at which fine crystals first appeared noted. The rate of cooling

was then recorded, in order that any subsequent "arrest" might be detected; and stirring was continued until brought to a stop by the accumulation of solid matter in the tube. The separation of the eutectic was usually preceded by overcooling, but the maximum temperature following crystallisation could be observed easily. The observations were repeated after remelting carefully the contents of the tube before these had cooled to the transition temperature at 84·2°, where an expansion occurs which often bursts the tube.

The results, which generally agreed within 1° in the case of the initial freezing points, and within one- or two-tenths of a degree in the case of the eutectic arrests, are given in Table I and are shown graphically in Fig. 1.

FIG. 1.



Equilibrium diagram for $NH_4 \cdot NO_3$ and $NaNO_3$.

TABLE I.

Initial and Final Freezing Points for Mixtures of Ammonium Nitrate and Sodium Nitrate.

Percentage of sodium nitrate.	Initial freezing point.	Eutectic arrest.	Percentage of sodium nitrate.	Initial freezing point.	Eutectic arrest.
0·0	169·6°	None	18·5	124·3°	120·8°
		observed.	20·0	121·9	120·8
5·0	156·5	None	22·0	124·8	120·8
		observed.	23·0	126·6	120·6
10·0	144·2	None	23·5	129·1	120·7
		observed.	25·0	133·4	120·8
15·0	132·0	120·6°	30·0	147·0	120·2
17·5	126·3	120·6	40·0	174·2	119·0

The composition of the mixture of ammonium and sodium nitrates of lowest melting point, as deduced from the curve, is as follows:

Ammonium nitrate . . .	79·5 per cent.
Sodium nitrate . . .	20·5 ,, ,,

The constant freezing point of this mixture may be taken as 120·8°, which is the mean of the six highest values recorded in Table II. The lower values are probably less accurate on account of the liability to overcooling, more especially in mixtures the compositions of which are more removed from that of the eutectic.

Melting Point of the δ-Form of Ammonium Nitrate.

Fig. 1 is interesting in two respects, (i) in the straightness of the branches, and (ii) in the presence of a distinct break in the left-hand branch at about 126°, corresponding with the transition temperature at 125·2°. Zawidski records a similar break at about 125° in the curve showing the initial crystallising points of mixtures of ammonium nitrate and silver nitrate. The latter diagram shows two eutectic points connected by a convex curve, corresponding with the separation of the compound $NH_4{\cdot}NO_3,AgNO_3$; but the two intersecting lines which show the separation, above and below 125°, of the ε- and δ-forms of ammonium nitrate, and the line which shows the separation of silver nitrate at concentrations above 50 mols. per cent. $AgNO_3$ have the same rectilinear form as the three sections of the freezing-point curve in Fig. 1. If the line between 125° and the first eutectic point (101·5°) on Zawidski's curve is produced back to the temperature axis, it cuts this at about 155°; similar treatment of the corresponding (but shorter) branch in Fig. 1 gives an intercept at 156° approximately. The experimental evidence appears therefore to justify the view that the extension of this branch to cut the ammonium nitrate axis, as shown by a broken line in Fig. 1, would give the temperature at which the metastable δ-form of ammonium nitrate would separate from the molten salt, and that the melting point of this form, which is ordinarily stable only between 84·2° and 125·2°, would be at 155—156°, if it could be heated to this temperature without undergoing polymorphous change.

Experiments on the Isopolymorphism of Ammonium and Sodium Nitrates.

The univalent nitrates are remarkable for their readiness to appear in several crystalline forms. Thus, ammonium nitrate is pentamorphous; lithium, rubidium, and thallium nitrates are trimorphous; potassium, cæsium, and silver nitrates are dimor-

phous; and *sodium nitrate alone does not exhibit polymorphism.* The crystalline forms in which the various nitrates are known are set out below, together with the transition temperatures at which the various forms change into a new form on cooling.

	Am.	Tl.	Li.	Na.	K.	Ag.	Rb.	Cs.
Melting point	170°	205°	253°	312°	336°	209°	?	414°
?	—	—	—	—	—	—	ζ 219°	—
Cubic	ε 125·2°	ε 142·5°	ε	—	—	—	ε 161°	ε 161°
Tetragonal ...	δ 84·1°	—	—	—	—	—	—	—
Rhombohedral	γ* 32·1°	γ 72·8°	γ	γ	γ 126°	γ 159·6°	γ	γ
Orthorhombic	β — 16°	—	β	—	β	β	—	—
Tetragonal ...	α —	—	—	—	—	—	—	—

* Perhaps monosymmetric.

Although *sodium nitrate is known only in one form*, this belongs to a system in which every one of the eight nitrates crystallises, with the possible exception of ammonium nitrate. It might therefore be expected that it would form isomorphous mixtures with most of the other nitrates; but there is in fact no case in which a complete series of isomorphous mixtures of sodium nitrate with another nitrate is known. Thus, silver nitrate forms two series of isomorphous mixtures, giving rise to a broken freezing-point curve (Hissink, *Z. physikal. Chem.*, 1900, **32**, 537). In the case of potassium nitrate, two series of isomorphous mixtures are also formed, containing up to 12 per cent. of KNO_3 or 20 per cent. of $NaNO_3$, but these form a eutectic mixture with one another (Hissink, *loc. cit.*). With thallium nitrate and lithium nitrate, no isomorphous mixtures appear to be formed.

Ammonium nitrate, on the other hand, forms a complete series of solid solutions with thallium nitrate, giving rise to a continuous freezing-point curve, corresponding with the separation of cubic crystals throughout. These crystals break up when the ammonium nitrate changes into the tetragonal form; but since the transition points of ammonium nitrate at 84° and of thallium nitrate at 80° are mutually lowered when both salts are present, it is probable that the rhombohedral and the orthorhombic forms of the two salts may also be isomorphous (Boks, *Diss.*, Amsterdam, 1902). Potassium nitrate, on the other hand, lowers the transition point at 32° (Müller, *Z. physikal. Chem.*, 1899, **31**, 354), showing that this salt is isomorphous with ammonium nitrate in the rhombohedral γ-form, but tends to separate from it on passing to the orthorhombic β-form; this fact is important, since ammonium nitrate, when prepared from Chile saltpetre, carries down with it most of the potassium nitrate of the raw material.

No complete investigation appears to have been made of the possible isopolymorphism of the ammonium and sodium salts.

The results of our experiments on the temperature of arrest of cooling in mixtures of ammonium and sodium nitrates are set out in Table II.

TABLE II.

Arrest Points in Mixtures of Ammonium Nitrate and Sodium Nitrate.

Percentage of sodium nitrate.	Arrests in cooling from ϵ to δ.	δ to γ.	γ to β.
(*a*) *Anhydrous salts.*			
0	125·2°	84·2°	32·2°
5	125·4	83·6	—
10	125·5	83·3	31·6
20·5	—	82·0	31·4
25	—	82·5	—
(*b*) *In presence of water.*			
Pure $AmNO_3$	—	—	31·5
+ 10% $NaNO_3$	—	—	31·45
+ 0·5% KNO_3	—	—	30·2

The transition temperatures of the anhydrous mixtures of salts were determined on blocks which had crystallised from the "melt," and were therefore subject to much more overcooling than in the case of the sludge of powdered ammonium nitrate with an organic liquid which was used in determining the transition temperatures of the pure salt. It will be seen that the arrest at 125·2° is not lowered by the presence of sodium nitrate, up to 17 per cent. of $NaNO_3$, where this arrest falls below the melting point of the mixture. The arrest at 84·2° is lowered by about a degree, but this is no more than the lowering by overcooling in pure ammonium nitrate when allowed to cool as a block instead of as a sludge. It is therefore clear that neither the ϵ- nor the δ-form of ammonium nitrate takes up enough sodium nitrate from the melt to affect its transition into the δ- or γ-form on cooling.

The experiments on the cooling of blocks from the melt do not, however, afford any real information as to the possible isomorphism of sodium nitrate with γ- or β-ammonium nitrate, since if these two salts crystallise from the melt as separate phases they will remain separate at lower temperatures, and no alteration of the 32° transition point can be expected. In order to get the ammonium nitrate to crystallise out in the γ- or β-form from a mixture containing sodium nitrate it is necessary to make use of a solvent. A sludge of ammonium nitrate and water was therefore cooled from about 80° and its transition temperature at 32° determined as in Müller's experiments on potassium nitrate (*loc. cit.*). The use of alcohol instead of water in making the sludge increased the overcooling, and no improvement was effected by adding ammonia; but a definite diminution of overcooling was effected by adding

nitric acid to the water used in making the sludge. The table shows an overcooling of 0·6° in the case of pure ammonium nitrate, but this was only increased by 0·05° by the presence of 10 per cent. of sodium nitrate, whereas 0·5 per cent. of potassium nitrate lowered the transition temperature by 1·3°. It is therefore clear that sodium nitrate is not isomorphous with the γ-form of ammonium nitrate; and since it is well known that ammonium nitrate does not carry down sodium nitrate when it separates from water below 32°, there is also no isomorphism with the β-form of the salt.

Summary.

1. An equilibrium diagram has been plotted for ammonium nitrate and sodium nitrate from 0 to 40 per cent. of $NaNO_3$.

2. The freezing-point curve consists of three accurately rectilinear sections corresponding with the crystallisation of two forms of ammonium nitrate and the one form of sodium nitrate.

3. If the line which shows the temperature of crystallisation of the δ-form of ammonium nitrate is produced, it cuts the axis of temperature at + 156°. A similar value can be deduced from the freezing-point diagram for ammonium nitrate with silver nitrate. This temperature may therefore be taken as the melting point of the metastable δ-form of ammonium nitrate.

4. The eutectic point for the two salts has been located at 120·8°, and 20·5 per cent. of sodium nitrate.

5. No evidence of isomorphism between the two salts has been discovered.

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CXII.—*Castelin, a New Glucoside from* Castela Nicholsoni.

By LOUIS PIERRE BOSMAN.

Castela Nicholsoni (Torrey and Gray) belongs to the natural order of *Simarubaceæ*. It is also known as "Chaparro Amargosa" or "Bitter Bush." The *Simarubaceæ* are well represented in Mexico, Texas, Guiana, and Venezuela, on the one hand, and also in China, India, and Australia, on the other. In China, there are no fewer than five representatives of the genus *Brucea* (Power and Lees, *Pharm. J.*, 1903, [iv], **17**, 183). There seems to have been some doubt as to the exact botanical classification of this shrub; but that of Torrey and Gray (*Castela Nicholsoni*) has been

accepted by Nixon (*J. Amer. Med. Assoc.*, 1916, **61**, 946), and by Watson and McIver (*J. Pharm. Expt. Ther.*, 1913, **11**, 331).

The natives of China, Mexico, and Texas have for centuries past used decoctions of the *Simarubaceæ* as remedies for dysentery, rabies, yellow fever, and malaria. The medicinal value of these herbs attracted the attention of the physicians in Texas (*loc. cit.*) and of Sherpheard and Lillie (*Prescriber*, 1918, 96).

Up to the present nothing has been published as to the chemical nature of the active principle of *Castela Nicholsoni*. Putegnaht is reported to have isolated a glucoside many years ago, but this report has been refuted (presumably by himself) (*New Remedies*, 1883, **12**, 102). A glucoside is, however, present, and the author proposes to assign to it the name *castelin*, and *castelagenin* to its product of hydrolysis.

Associated with castelin there is a "bitter principle," to which the author assigns the name *castelamarin*. The bark of *Simaruba amara*, of the same natural order, also contains a bitter principle, which is of therapeutic value. Gilling (*Pharm. J.*, 1908, [iv], **26**, 510) assigned the formula $C_{22}H_{30}O_9$ to it.

EXPERIMENTAL.

The herb may be extracted by continuous aqueous or alcoholic percolation. On concentration of the extract, castelamarin separates, and on concentration of the mother-liquor, castelin is obtained.

Castelin is purified by repeated crystallisation from water, from which it separates in long, white needles containing $3H_2O$, m. p. 205° (anhydrous). It dissolves in 85 parts of water at room temperature, and in 25 parts at 100°. It is more soluble in ethyl alcohol or cold concentrated hydrochloric acid, and gives a deep violet coloration with concentrated sulphuric acid. The anhydrous substance is very hygroscopic, taking up 8 per cent. of its weight of water on exposure to air for one hour (Found : H_2O at 120° = 14·4. $C_{15}H_{22}O_8,3H_2O$ requires H_2O = 14·1 per cent. Found : in anhydrous material, C = 54·7, 54·7; H = 6·7, 6·8. $C_{15}H_{22}O_8$ requires C = 54·6; H = 6·7 per cent.). The molecular weight was determined in boiling ethyl alcohol (Walker-Lumsden apparatus : $w = 1·2124$, $v = 15·5$, $\Delta t = 0·035°$; whence $M = 342$. Calc., $M = 330$).

Castelin is dextrorotatory, having $[\alpha]_D + 62·9°$ in aqueous solution.

Hydrolysis of Castelin.—Castelin is readily hydrolysed by dilute acids and alkalis; 20 per cent. hydrochloric acid is the most satisfactory hydrolysing agent. The yield is rather low (20 per cent.)—in one case only did it exceed this. Two grams of castelin are

boiled under reflux for two and a half hours with 40 c.c. of 20 per cent. hydrochloric acid, and *castelagenin* separates in large, colourless prisms, a further quantity being deposited if the solution is kept over-night; the total yield is 0·4142 gram.

Castelagenin is readily soluble in boiling glacial acetic acid, from which it crystallises in a pure condition. It is insoluble in chloroform, ether, or acetone, but freely soluble in warm methyl or ethyl alcohol. It melts at 240—241°, and gives no coloration with concentrated sulphuric acid (Found: C = 64·5, 64·4; H = 6·8, 6·9. $C_9H_{12}O_3$ requires C = 64·3; H = 7·1 per cent. Found: in boiling alcohol [$w = 0·3606$, $v = 42$, $\Delta t = 0·07°$], $M = 191$. Calc., $M = 168$).

As castelagenin is soluble in cold phenol, attempts have been made to verify this result cryoscopically. The average of a series of determinations is 90. This is in accordance with the experience of Seel and Kelber (*Ber.*, 1916, **49**, 2364), who, for aloin and some of its oxidation products, found cryoscopically in phenol solution only half the correct molecular weights, which were obtained ebullioscopically in acetone and in ethyl alcohol.

Castelagenin is dextrorotatory, $[\alpha]_D + 59°$. Its reactions with sodium hydroxide and sodium carbonate indicate that it is lactonic in nature. On oxidation with 30 per cent. nitric acid at 150°, castelagenin yields a minute quantity of a crystalline acid, m. p. 128—129°, which is moderately soluble in ether, gives the fluorescein reaction, and appears to be a dicarboxylic acid. Oxidation with acid or alkaline permanganate yields a similar product. A very little quantity of castelin being available, the oxidation product of castelagenin was obtained in so small amount that no definite conclusions could be drawn as to its chemical nature. For the present, the author can only state that he strongly suspects it to be a substituted succinic acid.

Castelagenin has been subjected to fusion with potassium hydroxide, to bromination, and to methylation. A careful examination of the products, however, reveals nothing definite.

The mother-liquor of the castelagenin has been examined as to the nature of the sugar (or sugars) which is formed on the hydrolysis of castelin. The osazone has been prepared, and recrystallised from pyridine. The crystals are identical in shape with those of glucosazone, and melt at 207—209°. A quantitative estimation of the glucose does not yield concordant results.

In conclusion, the author takes this opportunity of thanking Prof. Geo. Barger, F.R.S., for his interest and assistance in this research. The author is also very grateful to the Department of

Scientific and Industrial Research for the financial assistance rendered while he was doing research work at the Edinburgh University.

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CXIII.—*Polymorphism of Arsenic.*

By PORPHYRY NICOLAEVITCH LASCHTSCHENKO.

ARSENIC, like phosphorus, is known in three modifications: two crystalline, yellow and metallic arsenic, and one amorphous. The last variety has been least investigated. It is produced from yellow arsenic under the influence of light, by reduction of arsenious oxide, and also by sublimation of metallic arsenic. In the last method of preparation, there appear in order a mirror-like deposit, dark brown specks, and a grey crust, this being most remote from the source of heat.

The majority of authors deny the existence of two modifications of amorphous arsenic. Erdmann and Reppert (*Annalen*, 1908, **361**, 6) regard brown arsenic as the amorphous variety, of density (at 15°) 3·70, and deem the grey one an individual crystalline modification, of density 4·64. Besides difference in form, colour, and density, Erdmann ("Lehrbuch der anorganischen Chemie," 1910, p. 370) attributes to them different molecular compositions—As_8 for the brown, and As_2 for the grey arsenic—and gives 180° as the transition point of the brown and the grey forms.

According to Bettendorf (*Annalen*, 1867, **117**, 110) and Engel (*Compt. rend.*, 1883, **96**, 497, 1314) amorphous arsenic at 360° is transformed irreversibly and with considerable development of heat into the metallic form; Erdmann and Reppert (*loc. cit.*) refer the same point to 303°. Jolibois (*Compt. rend.*, 1911, **152**, 1767) and Gaubeau (*ibid.*, 1914, **158**, 121) determine the point of irreversible transformation both of brown and grey arsenic at 270—280°.

Discrepancies such as these, and the want of definite knowledge of the temperature and the heat of transition of metallic arsenic into the yellow modification, and also of the amorphous into the metallic form, furthermore, the interest attaching to the comparatively little investigated irreversible (monotropic) type of transformation, and the uncertainty of the data concerning the heat of fusion of arsenic, all these led the author to investigate the polymorphism of arsenic. The method adopted, consisting in the determination of the amount of heat evolved during the

cooling of a polymorphous substance, sealed in a quartz-glass tube, from various high temperatures down to that of the calorimeter, was first employed by Le Chatelier (*Compt. rend.*, 1908, **147**, 58) and has been described in detail in the author's previous papers (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1604; 1911, **43**, 793; 1913, **45**, 552; 1914, **46**, 311).

Experimental.

The metallic arsenic used was purified by sublimation in a vacuum. Its density, $d_{15^\circ}^{15^\circ}$ 5·7301, was in fair agreement with the values recorded in the literature (Moissan, "Traité de chimie minerale," I, 808). The amorphous arsenic was prepared by reduction with tin of arsenious oxide dissolved in concentrated hydrochloric acid, its density, $d_{15^\circ}^{15^\circ}$ 3·693, was determined pyknometrically in a mixture of spirit and water.

The results of measurements of the heat evolved on cooling are given in Tables I and II; in the first column are given the temperatures to which the arsenic had been heated, and in the second the amounts of heat (Q) evolved during the cooling of 1 gram of arsenic.

TABLE I.

Heat evolved on cooling of metallic arsenic. The highest temperature of the calorimeter = 11—12°.

Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).
173°	17·25	308°	25·27	435°	35·08	682°	57·75
196	18·19	317	26·58	450	35·14	714	62·06
216	19·25	332	27·00	475	37·92	738	62·63
217	19·96	354	27·67	538	44·07	750	72·61
250	21·54	376	28·90	595	50·61	775	74·60
258	21·92	400	30·82	628	53·44	822	76·46
300	25·00	414	34·00	659	57·31	868	136·76
						895	168·05

TABLE II.

Heat evolved on cooling of amorphous arsenic. The highest temperature of the calorimeter = 14—15°.

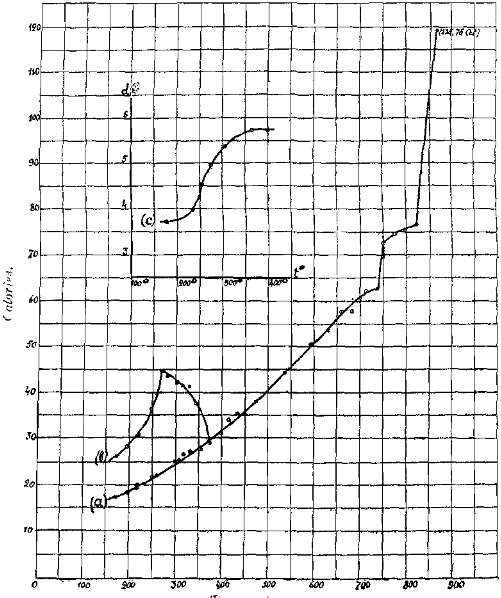
Temp.	Q (cal.).	Temp.	Q (cal.).	Temp.	Q (cal.).
173°	26·30	270°	44·68	330°	41·31
194	28·28	283	43·67	345	37·58
221	30·44	304	42·26	372	30·15
248	36·24	315	41·50		

The curves expressing the relation between the amount of heat evolved and the temperature are represented in Fig. 1.

In the case of metallic arsenic (*a*) a break in the curve occurs at 738—750°, and between 822—868° a sudden increase in the amount of heat evolved, owing certainly to fusion of arsenic, is to be noted. The first observations of the melting point of arsenic

were made by Landolt (1859) and Mellet (1872), who located this temperature between the melting points of antimony and silver (Moissan, *op. cit.*). In good agreement with this is Jonker's statement (*Z. anorg. Chem.*, 1909, **62**, 91) that arsenic heated in a sealed quartz-glass tube does not show any sign of fusion at 800°. How-

Fig. 1.



Temperature.

ever, Guntz and Broniewski (*Bull. Soc. chim.*, 1907, [iv], **1**, 977) deny the definite fusion point of arsenic. Schemtschuschny (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1463) found that arsenic melts at about 624°. Other melting points recorded are 480° by Erdmann (*op. cit.*), 850° ± 10° by Jolibois (*loc. cit.*), and 817° by Gaubeau (*loc. cit.*). The value deduced from measurements of

the heat evolved on cooling (Fig. 1, *a*) is in good agreement with the last two observations.

The latent heat of fusion of arsenic is unknown, and a particular difficulty attends its determination. When sublimed in a sealed tube, arsenic melts when its boiling point does not coincide with the temperature of fusion; in other words, at this temperature we have to deal with a triple point in the system: solid, liquid, and gaseous arsenic. Above this point, we have in a sealed tube a liquefied vapour of arsenic. At temperatures above 868° (Table I) the heat evolved on cooling increased very rapidly and irregularly and the experiments had to be discontinued because the tubes burst when placed in the calorimeter, diffusing a strong smell of garlic. This observation is noteworthy, as this characteristic smell is evidence of the presence of yellow arsenic.

Bettendorf (*loc. cit.*) observed the formation of the yellow modification when metallic arsenic was heated at a temperature near the melting point, but more exact information is wanting; the curve in Fig. 1 locates this point of transition of metallic into yellow arsenic between 738° and 750°, where the heat change amounts to about 7 calories per gram. The heat change at 624° observed by Schemtschuschny (*loc. cit.*), who heated arsenic above 700°, is probably attributable to this transition, for it cannot, as he supposed, be due to heat of fusion.

Turning to the curve for amorphous arsenic (Fig. 1, *b*) it is at once evident that its general form is typical of monotropic transformation. The same type of curve was obtained (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 793) in investigations of the transformation of aragonite into calcite. In this case, the quantities of heat given out by aragonite and calcite on cooling from about 400° are practically identical. At 445°, however, a distinct separation of the curves occurs; the heat evolved on cooling of aragonite increases rapidly until the temperature reaches 460—465°, but at 470° the curve again coincides with that of calcite. The attempt to trace the portion of the curve from the maximum to the points of coincidence failed, but here, on the curve for amorphous arsenic, a series of intermediate points was observed, furnishing evidence of the gradual transformation.

The change was also indicated by determinations of the density of amorphous arsenic which had been heated in sealed quartz-glass tubes and rapidly cooled to 15°. The results are as follows:—

Temp.	15°	175°	235°	255°	275°	305°	365°	400°
$d_{15°}^{15°}$	3·693	3·698	3·974	4·493	4·947	5·365	5·731	5·729

The corresponding curve (Fig. 1, *c*) is continuous, becoming horizontal at 360°. At 270—280° the density of amorphous

arsenic is equal to that of the grey modification, and at 360° to that of the metallic form.

The temperatures of transformation of amorphous arsenic into metallic arsenic recorded by Engel (360°) and hy Jolihois and Gaubeau (270—280°) (see above) *correspond respectively with* the maximum point and the point of coincidence on the curve *b* (Fig. 1).

The questions now arise, Which of these points is the transition temperature ? What is the nature of amorphous arsenic ? What is the way *of its irreversible and exothermic transformation into* the metallic modification ?

The close analogy between the polymorphism of arsenic and phosphorus suggests at once that, as in the case of red phosphorus (Cohen and Olie, *Z. physikal. Chem.*, 1910, **71**, 1), amorphous *arsenic is a solid solution of the yellow and metallic forms.* This view is supported not only by the change of density of amorphous arsenic with temperature (see above), but also by Engel's experiments (*loc. cit.*) on its sublimation. He found that the sublimation temperature of amorphous arsenic in a vacuum is 260°, whilst that of metallic arsenic is 450° (Conechy) or 616° (Jonker); at 360° sublimation ceases, but transformation of the amorphous into the metallic form may be effected by sufficiently prolonged sublimation at 310°. The deduction from these observations, which are analogous to those of Chapman for red phosphorus (Cohen and Olie, *loc. cit.*, p. 16), is that distillation of the more volatile component of a solid solution occurs and that metallic arsenic, which is non-volatile at this temperature, remains. In favour of this supposition is the fact that the density of hrown (3·7) and grey (4·6) arsenic is the mean of the densities of the yellow (2·0; Erdmann) and metallic (5·7) forms.

The transformation of amorphous arsenic into metallic arsenic is, however, quite irreversible and consequently the most important feature of the supposed dynamical allotropy—$As_{yellow} \rightleftarrows As_{met.}$—namely, the reversibility, is absent.

Erdmann's hypothesis, that brown arsenic passes into the metallic form with intermediate production of the grey modification at 180°, the metallic form being ultimately obtained at 303°—$As_8 \longrightarrow As_2 \longrightarrow As_2$—is not tenable because first, there is great doubt as to the existence of a critical point at 180° for amorphous arsenic, and, secondly, the hypothesis that such compositions may be assigned to the brown, grey, and metallic modifications of arsenic itself needs proof.

The relation between amorphous and metallic arsenic therefore remains an open question. The solution of the problem

would, however, appear to be closely connected with our conceptions of the amorphous state of matter. The modern colloid chemist denies the existence of an amorphous state of matter. In his view, amorphous substances are constituted of indefinitely crystalline individuals that have not yet attained their full form. Such "cryptocrystalline" structure, which is optically indetectable, has been attributed by some authors (Retgers, Linck, Cohen, Erdmann) both to amorphous arsenic and amorphous (red) phosphorus. However this may be, there is no doubt that the amorphism of brown arsenic, as well as of red phosphorus, is, not *its primary*, but *its secondary state*; *the first product of the action of light on yellow arsenic or white phosphorus is colloidal.* So also, amorphous arsenic is prepared by a method of reduction favourable to sol formation, and in the presence of stannous chloride the coagulation of this sol to dark brown flakes with a red tint can be observed. With regard to the grey variety, it is remarkable that it always appears as the secondary phase in the formation of amorphous arsenic. In this connexion Engel's remark (*loc. cit.*) deserves particular attention: grey arsenic is similar to the brown, but is composed of less dispersed particles. This is the more probable, since brown arsenic is to some extent soluble in carbon disulphide (Erdmann, *loc. cit.*), whereas the grey modification is quite insoluble. Regarded from this point of view, grey arsenic is not an allotropic modification at all, but is merely a stage in the continuous passage of arsenic from the colloidal state to the crystalline, a phenomenon observable in a number of cases and realisable experimentally (Janek, "Textbook of Colloid Chemistry," Petrograd, 1915, pp. 141—150). The production of grey arsenic from the brown form by heating is a step in the process; it occurs, as has been shown, just when the vapour pressure of amorphous arsenic becomes determinable and sublimation begins.

It was mentioned above that Erdmann records 303° as the temperature of transformation of amorphous arsenic, as at this temperature electrical conductivity becomes apparent in the amorphous modification. Repeating these experiments, the author found that this point depends on the conditions of heating and on the form and the distance apart of the electrodes, and is determined by the formation on the inner walls of the electrolytic tube of a very thin, mirror-like deposit by means of which contact is made; the contents of the tube consist of a baked, brittle, dark-grey mass, of density almost equal to that of grey arsenic. Thus, together with sublimation of amorphous arsenic in a sealed tube, there is the appearance of the first minute crystals of the metallic

form. This occurs at 270—280°, the maximum point on the curve *b* (Fig. 1). Above this temperature, the transformation proceeds by distillation of the metastable phase of the amorphous arsenic and condensation of the vapour in the form of the stable metallic modification. This continues up to 360°, at which temperature sublimation of the metastable phase ceases and the process of irreversible and exothermic transformation is practically finished.

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CXIV.—*Organo-derivatives of Tin and Lead. Part I. Application of Lead and Tin Tetraphenyls in the Preparation of Organo-metallic Compounds.*

By ARCHIBALD EDWIN GODDARD, JULIUS NICHOLSON ASHLEY, and RICHARD BROMLEY EVANS.

IT has recently been shown (Goddard and Goddard, this vol., p. 256) that lead and tin tetraphenyls can be used for the preparation of thallium diphenyl chloride, and experiments have now been carried out with the object of ascertaining whether this type of reaction could be utilised in the preparation of organo-metallic componnds which are difficult to isolate by the usual methods.

Lead tetraphenyl and arsenic trichloride react to form diphenylarsenious chloride, according to the equation $Ph_4Pb + AsCl_3 = Ph_2PbCl_2 + Ph_2AsCl$. All previous methods used to obtain this compound yield it only as a by-product (Michaelis and La Coste, *Annalen*, 1880, **201**, 196; Michaelis and Link, *ibid.*, 1881, **207**, 195; Michaelis and Reese, *Ber.*, 1882, **15**, 2873; Roeder and Blasé, *ibid.*, 1914, **47**, 2750).

The tendency shown by arsenic to give mono- or tri-aryl compounds, and not diaryl derivatives, is again in evidence with antimony. The latter type of compound has now been obtained directly by the following reactions: (1) $Ph_4Pb + SbCl_3 = Ph_2PbCl_2 + Ph_2SbCl$, (2) $Ph_4Pb + SbCl_5 = Ph_2PbCl_2 + Ph_2SbCl_3$ (compare Michaelis and Reese, *Annalen*, 1886, **233**, 58; Hasenbäumer, *Ber.*, 1898, **31**, 2911).

A similar reaction takes place with bismuth bromide, lead diphenyl chloride and diphenylbromobismuthine resulting; the latter compound has been previously obtained by Michaelis and Marquardt (*Annalen*, 1889, **251**, 327) by the interaction of bismuth bromide and triphenylbismuthine.

Of the chlorides of Group VI, tellurium tetrachloride was the only one to yield definite products, tellurium diphenyl chloride and lead diphenyl chloride being obtained (compare Krafft and Lyons, *Ber.*, 1894, **27**, 1761; Lederer, *Ber.*, 1911, **44**, 2287; *Annalen*, 1912, **391**, 326).

The interaction of lead tetraphenyl and stannic chloride, and subsequent treatment with water, lead to the production of lead diphenyl chloride, tin diphenyl hydroxychloride and oxide; but stannous chloride reacted as follows: (1) $Ph_4Pb + 2SnCl_2,2H_2O = Ph_2PbCl_2 + Ph_2SnCl_2 + Sn + 2H_2O$, (2) $Ph_2SnCl_2 + H_2O = Ph_2SnCl{\cdot}OH + HCl$, (3) $Sn + 2HCl = SnCl_2 + H_2$. Tin tetraphenyl and stannic chloride, when caused to react as above, gave a theoretical yield of tin diphenyl hydroxychloride (see Aronheim, *Annalen*, 1878, **194**, 145).

The following compounds gave no products with lead tetraphenyl under the same conditions of experiment: phosphorus tri- or penta-chloride, mercuric or lead chloride, thionyl or acetyl chloride, although in the latter case heat was developed, nor were derivatives isolated from tin tetraphenyl and the chlorides of mercury or sulphur.

Polis (*Ber.*, 1887, **20**, 3331) showed that lead tetraphenyl, when boiled for some time with acetic acid in benzene solution, gives rise to lead diphenyl acetate, but the authors have failed to obtain the same result with tin tetraphenyl. By the action of propionic and valeric acids in xylene solution, *acid lead diphenyl propionate* and *lead diphenyl valerate* were isolated. Only unchanged lead tetraphenyl was recovered when *n*-hexoic, *n*-octoic, mono- or di-chloroacetic acid was used, and lead diphenyl oxide did not react with citric or tartaric acid. The following salts were isolated: *acid lead diphenyl trichloroacetate, oxalate, iodate,* and p-*nitrobenzoate*. Other investigations of this type are being carried out in the aliphatic series, and also with mixed tetra-alkyls, tetra-aryls, and alkyl aryls of tin and lead.

EXPERIMENTAL.

All the yields given in the following experiments are based on the weight of metallic chloride used.

Diphenylarsenious Chloride.—Three grams of lead tetraphenyl and 1·13 grams of arsenic trichloride in 30 c.c. of toluene were heated under reflux for one hour, and after standing for twelve hours the solution was again warmed and filtered. The residue (2·34 grams) consisted of lead diphenyl chloride, and evaporation of the filtrate gave 1·5 grams of an oil, identified as diphenylarsenious chloride (yield 91 per cent.). From the latter, by

chlorination and twice recrystallising from benzene, crystals of diphenylarsenious trichloride, m. p. 174°, were obtained.

Diphenylstibine Chloride.—Lead tetraphenyl (3·27 grams) and 1·44 grams of antimony trichloride were heated under reflux with 5 c.c. of toluene for half an hour, when a solid mass resulted, which was treated with a further 15 c.c. of toluene and heated again. After cooling and filtering, 2·55 grams of residue, melting above 280°, were obtained (lead diphenyl chloride), whilst the filtrate, after removal of the toluene, gave 1·81 grams of diphenylstibine chloride in the form of an oil (yield 92 per cent.). The latter product was chlorinated in dry ether and the mass recrystallised from hydrochloric acid, when diphenylstibine trichloride, m. p. 176°, was isolated.

Diphenylstibine Trichloride.—A mixture of 2·88 grams of lead tetraphenyl and 1·67 grams of antimony pentachloride in 50 c.c. of carbon tetrachloride was boiled for one hour, then filtered hot. The residue (3·87 grams), which did not melt completely at 180°, was boiled with hydrochloric acid and filtered; lead diphenyl chloride (2·4 grams) remained, and the hydrochloric acid filtrate deposited 1·3 grams of diphenylstibine trichloride, m. p. 176°. The carbon tetrachloride filtrate yielded a further 0·4 gram of the trichloride (total yield 81 per cent.).

Diphenylbromobismuthine.—Three grams of lead tetraphenyl and 2·61 grams of bismuth bromide were heated under reflux with 30 c.c. of chloroform for half an hour, and the mixture was filtered hot. The residue (1·28 grams) consisted of lead diphenyl bromide, and evaporation of the filtrate gave a residue, from which a further 1·4 grams was extracted, together with 1·95 grams of diphenylbromobismuthine, m. p. 157—158° (yield 75·4 per cent.).

Tellurium Diphenyl Chloride.—Tellurium tetrachloride (2·7 grams) and 5·2 grams of lead tetraphenyl in a mixture of 40 c.c. of toluene and 10 c.c. of xylene were boiled for one hour. After filtration, the residue was extracted with methyl alcohol, when 0·3 gram of tellurium diphenyl chloride was obtained. The solid left after this extraction (3·5 grams) was lead diphenyl chloride. The original filtrate on evaporation yielded 2·9 grams of solid, which were almost completely soluble in methyl alcohol, the solution depositing 1·47 grams of pure tellurium diphenyl chloride, m. p. 160—161°. The small quantity of substance insoluble in methyl alcohol appeared to be metallic tellurium. The above tellurium compound, on boiling with water, gave tellurium diphenyl hydroxychloride, m. p. 233—234° (yield 50 per cent.).

Action of Stannic Chloride on (a) *Lead Tetraphenyl*, (b) *Tin Tetraphenyl.*—(*a*) A mixture of 3·5 grams of lead tetraphenyl

and 1·72 grams of stannic chloride in 30 c.c. of toluene was boiled for forty minutes. After filtering, a residue of 2·9 grams of lead diphenyl chloride was obtained, and the filtrate, on evaporation and addition of boiling water, gave a small quantity of tin diphenyl hydroxychloride, m. p. 185°. On evaporation to dryness, 1·49 grams of tin diphenyl oxide remained.

(*b*) Tin tetraphenyl (1·5 grams) and 0·91 gram of stannic chloride were heated under reflux in xylene for three-quarters of an hour. The residue (0·11 gram) was inorganic, and the filtrate, after evaporation and treatment with water, yielded 0·93 gram of tin diphenyl hydroxide, m. p. 188°. The production of the latter being due to the added water, tin diphenyl chloride was evidently formed in the reaction.

Action of Stannous Chloride on Lead Tetraphenyl.—Three grams of lead tetraphenyl and 2·42 grams of stannous chloride ($+ 2H_2O$) in 30 c.c. of xylene were boiled for two and a half hours. The residue obtained after filtering was heated under reflux with absolute alcohol, and subsequent filtration gave 1·5 grams of a mixture of lead diphenyl chloride and stannous chloride, and the alcoholic filtrate gave a further 1·02 grams of the former compound. The xylene filtrate quickly deposited 0·46 gram of tin diphenyl hydroxychloride, m. p. 185°, and, when evaporated, 0·47 gram of tin diphenyl chloride, m. p. 42°.

Acid Lead Diphenyl Propionate.—One gram of lead tetraphenyl and 0·58 gram of propionic acid were heated under reflux in xylene for one hour, and the mixture was filtered. Evaporation of the filtrate gave fine needles (0·65 gram), which melted to a clear liquid at 168—169°, this decomposing at 230—235° (Found: C = 42·30; H = 3·87; Pb = 36·13. $C_{18}H_{20}O_4Pb,C_3H_6O_2$ requires C = 43·34; H = 4·51; Pb = 35·64 per cent.). The salt is completely soluble in alcohol, ether, chloroform, carbon tetrachloride, acetone, toluene, or pyridine, moderately soluble in ethyl acetate, and insoluble in light petroleum.

Lead diphenyl valerate forms white needles, m. p. 168—170° (Found: Pb = 36·73. $C_{22}H_{28}O_4Pb$ requires Pb = 36·78 per cent.). With the exception of its solubility in light petroleum, this salt has the same solubilities as the propionate.

Acid lead diphenyl trichloroacetate is a crystalline powder, which softens at 170—175° and decomposes rapidly at 210° without melting (Found: Pb = 26·99, 26·89. $2C_{16}H_{10}O_4Cl_6Pb,C_2HO_2Cl_3$ requires Pb = 26·99 per cent.). The salt is completely soluble in most organic solvents except carbon tetrachloride and light petroleum.

Lead diphenyl oxalate is a white, crystalline powder, which

darkens at 280°, and decomposes rapidly at 293—295° (Found: Pb = 43·26; H_2O = 5·64. $2C_{14}H_{10}O_4Pb,3H_2O$ requires Pb = 43·49; H_2O = 5·67 per cent.). The salt is slightly soluble in acetone, pyridine, or dilute sulphuric acid, and insoluble in other organic solvents.

Lead diphenyl iodate is a crystalline, buff-coloured powder (Found: Pb = 29·95, 29·54. $C_{12}H_{10}O_6I_2Pb$ requires Pb = 29·14 per cent.). The salt does not melt at 300°, and explodes when treated with concentrated sulphuric acid, iodine being liberated. It is slightly soluble in pyridine and insoluble in other organic solvents.

Lead diphenyl p-nitrobenzoate forms small, pale yellow needles, darkening and melting at 256° (Found: Pb = 29·39; N = 4·08. $C_{26}H_{18}O_8N_2Pb$ requires Pb = 29·88; N = 4·04 per cent.). The salt is moderately soluble in all organic solvents except ether and light petroleum.

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CXV.—*The System Potassium Sulphate–Aluminium Sulphate–Water at 25°.*

By HUBERT THOMAS STANLEY BRITTON.

No one appears to have worked out an isotherm of the system potassium sulphate–aluminium sulphate–water, although several investigators have made determinations of the solubility of alum (Poggiale, *Ann. Chim. Phys.*, 1843, [iii], **8**, 467; Mulder, *Scheik. Verhandel,* Rotterdam, 1864, 90; Locke, *Amer. Chem. J.*, 1901, **26**, 175; Berkeley, *Phil. Trans.*, 1904, *A*, **203**, 189; Marino, *Gazzetta,* 1905, **35**, ii, 351). Marino also determined the composition of the liquid phases which exist in equilibrium at various temperatures with two solid phases, namely, with crystals of either alum and potassium sulphate or alum and aluminium sulphate.

EXPERIMENTAL.

Methods of Analysis.—As the liquid phases contained aluminium sulphate and potassium sulphate only, the simplest method of analysis was to estimate the total sulphate and the alumina; from

the results, the amounts of the two salts could be calculated. The estimation of sulphate as barium sulphate in presence of aluminium salts was found to be quite trustworthy provided that plenty of hydrochloric acid (about 5 c.c. of the concentrated acid) was added in the cold to the dilute solution (about 500 c.c.). The method of estimating the alumina required a little consideration. The amounts to be estimated varied considerably, and in some cases they were so minute that weighable quantities would have been obtained only by the treatment of inconveniently large volumes of the liquid phases. Schmatolla (*Ber.*, 1905, **38**, 987) found that solutions of aluminium sulphate could be titrated with sodium hydroxide and phenolphthalein at 100°. With aqueous solutions of aluminium sulphate, his titrations were always low, sometimes as much as 0·7 per cent., but when the solution contained excess of barium chloride, he obtained accurate results. Scott (*J. Ind. Eng. Chem.*, 1915, **7**, 1059), however, found that titrations without barium chloride were satisfactory. The inaccuracy of Schmatolla's first method was due to some aluminium sulphate having been carried down by the aluminium hydroxide in the course of titration. Hence it was thought that if very dilute solutions of aluminium sulphate were employed, adsorption might be eliminated and the method rendered quantitative. The method was therefore investigated as follows. Several solutions (100 c.c.) of aluminium sulphate containing quantities of alumina ranging from 0·008 to 0·13 gram were titrated, while boiling, with $N/10$-sodium hydroxide and phenolphthalein, and accurate results were obtained. In the case of solutions which contained an amount of alumina greater than 0·1 gram, difficulty was experienced in determining the end-point exactly, owing to masking caused by the aluminium hydroxide precipitate. The presence of potassium sulphate in solution does not affect the accuracy of the method, which is, under the above conditions, an excellent one for the estimation of alum. Since the time when this method was tested and adopted by the author, two papers have appeared, one by Kolthoff (*Z. anorg. Chem.*, 1921, **112**, 172), who prefers the use of excess of barium chloride, and the other by Tingle (*J. Ind. Eng. Chem.*, 1921, **13**, 420), who found the method satisfactory either with or without the use of barium chloride. This method was employed throughout these determinations, usually in the absence of barium chloride. In the titration of very dilute solutions, the advantages accruing from the use of barium chloride were not apparent.

Equilibrium Determinations.—Saturated solutions (about 150 c.c.) of potassium sulphate and aluminium sulphate in varying propor-

tions were made at a temperature a few degrees above 25°. Great care was taken to keep the temperature of saturation as low as possible, otherwise considerable hydrolysis ensued and the solution became very turbid. These solutions were poured into bottles fitted with mechanical stirrers, placed in a thermostat regulated at 25·0 ± 0·1°, and were stirred until equilibrium between the liquid phases and solid phases which had crystallised out had been attained. Stirring of each liquid phase was generally continued for two or three days, the solid phase was then allowed to settle, and about 20 c.c. of the clear liquid phase were removed, weighed, made up to 250 c.c., and analysed. In order to ascertain whether equilibrium had been attained, the remaining liquid phase was again stirred for another period of at least a day with the solid phase and a further portion tested. The solid phase was filtered through a Büchner funnel and weighed portions were analysed. In the cases where the solid phase was alum, the crystals were well-defined and were consequently easily freed from the adhering mother-liquor. Hence there was no necessity of making a complete analysis; suitable quantities, however, were dissolved in water, and the solutions boiled and titrated in order to settle definitely the nature of the solid phase.

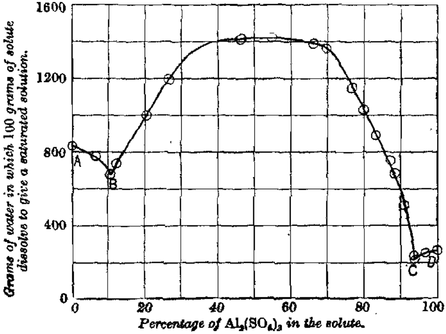
Although the method of allowing a slightly supersaturated solution to attain equilibrium at 25° gave satisfactory results for those liquid phases which were in equilibrium with alum, much difficulty was experienced in applying this procedure to those solutions which, it was believed, would on crystallisation attain equilibrium with either potassium sulphate or aluminium sulphate. For example, raising the temperature of a solution, the solute of which contained, say, 5 per cent. of aluminium sulphate and 95 per cent. of potassium sulphate, being therefore very dilute with respect to aluminium sulphate, produced considerable hydrolysis of the aluminium salt. Data obtained in such a way would correspond with the solubility of potassium sulphate in the sulphuric acid liberated. After that section of the curve indicating the composition of liquid phases in equilibrium with alum had been obtained, it was possible to make up at room temperature solutions which, when stirred with the appropriate solid phases, would attain equilibrium with them. This procedure was also adopted to obtain data for the two liquid phases, each of which was in equilibrium with two solid phases. The time required for the various phases, solid and liquid, to attain equilibrium in this way was much longer than in the case of the supersaturated solution; in some determinations several weeks were necessary.

Results.—The following data were obtained.

Liquid Phases. Percentage of K_2SO_4 in the solute.	Liquid Phases. Grams of water in which 100 grams of solute dissolve to give a *saturated* solution.	Solid phases.	Liquid phases. Percentage of K_2SO_4 in the solute.	Liquid phases. Grams of water in which 100 grams of solute dissolve to give a saturated solution.	Solid phases.
100	830	K_2SO_4.	23·3	1150	Alum.
93·4	773	,,	20·1	1028	,,
89·6	679	K_2SO_4 and alum.	16·9	886	,,
87·9	731	Alum.	12·8	754	,,
79·6	999	,,	11·4	685	,,
73·8	1190	,,	8·9	508	,,
53·7	1415	,,	6·5	235	,,
45·5	1424	,,	6·0	211	Alum and $Al_2(SO_4)_3$, $18H_2O$.
33·7	1384	,,	3·4	245	$Al_2(SO_4)_3$, $18H_2O$.
30·2	1362	,,	0	261	,,

The above results are represented graphically in Fig. 1, using a slightly modified form of the method first proposed by Jänecke (*Z. anorg. Chem.*, 1906, **51**, 132).

FIG. 1.



Each of the three branches of the diagram represents saturated solutions in equilibrium with one solid phase only, except those

solutions which are represented by the two points at which the curves intersect. The liquid phases corresponding with *AB*, *BC*, and *CD* are solutions saturated respectively with potassium sulphate, alum, and aluminium sulphate (with $18H_2O$). As the temperature is fixed, any point, except *B* and *C*, on the curves represents a system having one degree of freedom, namely, one of change in concentration. The points *B* and *C* represent liquid phases the compositions of which at 25° are fixed, each solution being in equilibrium with two solid phases—the former with potassium sulphate and alum, and the latter with alum and aluminium sulphate crystals.

If curves are drawn from data recorded in Marino's paper, showing the variation in composition of the solutes of these univariant liquid phases with temperature, it will be seen that the range of composition of solutes of saturated solutions in equilibrium with alum is considerably diminished on raising the temperature. Thus the range at 25° in 100 grams of solute is from 10·4 to 94·0 grams of aluminium sulphate (Fig. 1), which, incidentally, agrees with the figures obtained by extrapolation from Marino's results, whereas the range (as shown by the curves) at 60° is from 35 to 88 grams of aluminium sulphate. From the isotherm which has been worked out, Marino's data, and the variation of solubility of alum with temperature, a good general knowledge of the system under consideration may be obtained.

Although the percentage of hydrolysis of aluminium sulphate at 25° is comparatively low in the liquid phases involved in this work, appreciably turbid solutions were sometimes obtained, especially in those solutions the aluminium sulphate concentrations of which were great. As the effect of raising temperature is to enhance hydrolysis, it was decided not to investigate the system at a higher temperature.

The author desires to thank Professor Allmand for the interest he has taken in this work and also for valuable criticism and advice.

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CXVI.—*The Isotope Ratio of New Zealand Boron.*

By ALEXANDER DONALD MONRO.

ASTON (*Phil. Mag.*, 1920, [vi], **39**, 611) has shown that the element boron consists of two isotopes of atomic weight 10 and 11 respectively. In a lecture delivered before the Chemical Society (T., 1921, **119**, 682) the same worker suggested the study of the atomic weights

of elements derived from various mineral sources. This has been attempted in the case of boron.

The source of boron chosen for examination was the Hanmer Hot Springs in the South Island of New Zealand. The amount of boron in New Zealand is small, and this was one of the principal supplies available. The water from what is known as the "New Bore" in that locality contains 47·46 parts of borax per 100,000 (Reports of the Dominion Laboratory of New Zealand, 1913). The Hanmer Springs lie in a small intermontane basin at the foot of the seaward Kaikoura range. As this range is of at least Triassic age, and as the Hanmer Springs are deep-seated, the borax derived from this source must have been segregated since Triassic times.

In an examination of the equivalent weight of a substance from a special source it is obviously easier to determine the equivalent weight by a comparative method, using some standard sample of the substance as a basis of comparison. The standard used in these determinations was pure sodium tetraborate. This sample was found to be free from potassium, chlorine, and carbonate, and as a further precaution it was carefully recrystallised four times from water.

The isolation of boric acid from the mineral water proved troublesome and was not effected without considerable loss. The method of distillation with methyl alcohol was attempted, but involved considerable difficulties. It was therefore abandoned in favour of precipitation as silver borate, followed by decomposition with dilute hydrochloric acid, and crystallisation of boric acid from the solution. The boric acid thus obtained was fused with a slight deficit of pure sodium carbonate in a platinum crucible. The product was recrystallised six times from water, fused in a platinum crucible, and again recrystallised.

The method of determination chosen was a modification of the method of Rimbach (*Ber.*, 1893, **26**, 164), who titrated borax with hydrochloric acid, using methyl-orange as indicator. Fused sodium tetraborate was used instead of borax in this investigation. This method lent itself to comparative treatment better than that of Ramsay and Aston (T., 1893, **63**, 211).

The weights were standardised against a certified set which had been tested at the National Physical Laboratory. The pipette and burette were standardised by weight measurements. In the final operations "conductivity" water was employed, and the standard solution of hydrochloric acid was obtained by the method given by Richards and Wells (*Publication of the Carnegie Institute*, No. 28).

The following procedure was adopted in the determinations. About 2 grams of borax were fused in a platinum crucible, trans-

ferred immediately to a desiccator, and, when cold, allowed to stand for ten minutes in the (desiccated) balance case before weighing. The fused sodium tetraborate was then treated with a little hot "conductivity" water, and the solution carefully transferred to a beaker and made up to 50 c.c. The mass in the crucible was fused again and the weight of sodium tetraborate thus determined by difference. The solution was then titrated to a standard tint the same amount of methyl-orange being used in each case.

The results are expressed as the normalities of the hydrochloric acid solution employed :

First series.	Sodium tetraborate (Merck).		Second series.	Sodium tetraborate (Hanmer).	
Weight (gram).	C.c.	Normality $\times 10^5$.	Weight (gram).	C.c.	Normality $\times 10^5$.
0·4289	41·37	10287	0·2207	21·30	10282
0·1360	13·13	10278	0·1776	17·16	10270
0·1214	11·73	10268	0·1596	15·39	10290
0·6618	63·83	10287	0·1355	13·09	10272
0·2628	25·39	10270	0·2032	19·61	10281
0·2617	25·24	10288	0·1282	12·37	10283

Mean normality $\times 10^5 = 10279·7 \pm 2·5$. Mean normality $\times 10^5 = 10279·7 \pm 2·0$.

Assuming that the atomic weight of boron is 10·90 (Smith and van Haagen; *vide* Report of the International Committee on Atomic Weights 1919–1920), the molecular weight of sodium tetraborate is 201·60. The molecular weight of the New Zealand sample will be

$$201·60 \times \frac{10279·7 \pm 2·0}{10279·7 \pm 2·5}$$

that is, 201·60 $\pm$ 0·062.

The weight of four atoms of boron will be 43·60 $\pm$ 0·062, and the atomic weight of boron will be10·90 $\pm$ 0·0155. That is, the isotope ratio of New Zealand boron is the same as that of European boron within the limit one part in sixty.

In conclusion, I desire to express my thanks to Professor P. W. Robertson for the interest he has taken in this research, and for the excellent advice he has given during the work.

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CXVII.—*The Conversion of Allyl Alcohol to Glyceryl Chloro- and Bromo-hydrins.*

By JOHN READ and ERIC HURST.

IT is remarkable that, in spite of their early discovery and manifold applications, the chloro- and bromo-hydrins derived from glycerol are even yet by no means accurately known. A reference to the literature indicates, indeed, the existence of considerable uncertainty in regard to these derivatives (see, for instance, Beilstein, "Handbuch der organischen Chemie," 4th ed., 1920, I, 477). Even in the case of the readily accessible β-dibromobydrin, no trustworthy determination of density appears to have been made until comparatively recently (Forster and Withers, T., 1912, **101**, 496; Philip, T., 1912, **101**, 1868). As has already been indicated in references to other halogenohydrins (T., 1920, **117**, 1214; 1921, **119**, 1774), this position is largely due to the nature of the methods which have hitherto been utilised in preparing such substances. Like ethylenebromohydrin, the derivatives now under discussion have usually been prepared from the corresponding polyhydric alcohol by interaction with (1) the anhydrous halogen acid, or (2) a phosphorus haloid; the enhanced difficulty, in the case of a trihydric alcohol, of controlling such reactions so as to yield a well-defined product is manifest. Thus (1), Berthelot (*Ann. Chim.*, 1861, [iii], **61**, 296) prepared α-monochlorohydrin by the interaction of glycerol and hydrogen chloride at 100°, whilst Hanriot (*Ann. Chim.*, 1879, [v], **17**, 73) stated that the product contained a small proportion of β-monochlorohydrin which could be separated by fractional distillation under diminished pressure, the boiling points being 139°/18 mm. (α) and 146°/18 mm. (β). More recently, Nivière (*Compt. rend.*, 1913, **156**, 1628) prepared α-monochlorohydrin (b. p. 121·5—122·5°/15 mm.) by saturating glycerol with hydrogen chloride at 120—130°. The same reagents have also been used in preparing α- and β-dichlorohydrin (Fauconnier, *Bull. Soc. chim.*, 1888, [ii], **50**, 212). Further (2), Berthelot and de Luca (*Ann. Chim.*, 1856, [iii], **48**, 304) found that chlorides of phosphorus reacted with glycerol to give a mixture of mono- and di-chlorohydrins and epichlorohydrin, together with large amounts of other products. Similar methods have been applied in preparing the corresponding bromohydrins (Berthelot and de Luca, *loc. cit.*; Carré, *Bull. Soc. chim.*, 1910, [iv], **7**, 835).

Another principle (3), namely, that of direct addition of hypochlorous or hypobromous acid to a suitable unsaturated substance, has been utilised to some extent in other investigations of the kind

under notice. Henry (*Ber.*, 1870, **3**, 351; 1872, **5**, 449; *Rec trav. chim.*, 1897, **16**, 208) stated that allyl derivatives combinec readily with hypochlorous acid, but that in the case of allyl alcoho the yield of β-monochlorohydrin was small, owing apparently tc oxidation. The successful results which have attended the use o chlorine water and bromine water in the preparation of halogeno hydrins from unsaturated substances (T., 1917, **111**, 240; 1920 **117**, 359, 1214; 1921, **119**, 1774) led us to apply these reagents tc allyl alcohol under the customary conditions. In accordance witl the general principle which has been laid down for the mobil equilibrium involved, the product should consist of a mixture o monohalogeno- and dihalogeno-hydrin, resulting from the simul taneous occurrence of the two additive reactions indicated below:

$$\begin{array}{ccc} X_2 \quad + & HOH \rightleftharpoons HX & + \quad HOX \\ \downarrow & & \downarrow \\ CH_2X\cdot CHX\cdot CH_2\cdot OH & & HO\cdot CH_2\cdot CHX\cdot CH_2\cdot OH \\ (\beta\text{-Dihalogenohydrin}). & & (\beta\text{-Monohalogenohydrin}). \end{array}$$

From observations made in the study of similar processes of this type, it seemed likely that the main product of the reaction would be β-monohalogenohydrin (compare Henry, *loc. cit.*), and that the separation of this derivative from the accompanying β-dihalogenohydrin would be simple in comparison with the treatment o the complex mixtures which result from glycerol by the applicatior of principles (1) or (2).

Apparently the action of chlorine water on allyl alcohol has no been investigated hitherto, but its bromination in aqueous solution was undertaken by Markownikoff (*Jahresber.*, 1864, 490) for the preparation of β-dibromohydrin (βγ-dibromopropyl alcohol). Subsequently, Fink (*Monatsh.*, 1887, **8**, 562) showed that addition of hypobromous acid occurred in the reaction, and that as much as 45 per cent. of the bromine could be converted to hydrobromic acid. The reaction, which was more fully studied by Biilmann (*J. pr. Chem.*, 1900, [ii], **61**, 215), appears to be the only one on record, prior to the present series of investigations, in which the possibility was recognised of bromine water functioning effectively as a source of hypobromous acid.

The results of the experiments now described were such as to confirm the above-mentioned anticipations, but with chlorine water the process was complicated by the simultaneous occurrence of other reactions. In the case of bromine water, the results stand in close correspondence with those given by ethylene (T., 1920, **117**, 1214). The reactions thus yielded specimens of four definite halogenohydrins: namely, *β-monochlorohydrin*, *β-dichlorohydrin*,

β-monobromohydrin, and β-dibromohydrin. With the exception of β-dichlorohydrin, these appeared to be chemically pure, and in the majority of instances the observed physical constants, when compared with the somewhat scanty data at our disposal, were in agreement with this conclusion. For the preparation of the pure β-dihalogenohydrins, the halogenation of allyl alcohol in carbon disulphide solution, in the manner devised by Tollens (*Annalen*, 1870, **156**, 166; 1873, **167**, 224) and improved by Kohler (*Amer. Chem. J.*, 1909, **42**, 381), is to be recommended; but when the β-monohalogenohydrin is also required, the reactions now described should be of practical importance, particularly in preparing the bromine derivatives.

EXPERIMENTAL.

The Reaction between Allyl Alcohol and Bromine Water.

A large beaker, surrounded with melting ice and provided with a mechanical stirring apparatus, was charged with a solution of allyl alcohol (about 10 grams) in water (about 600 c.c.). On passing a current of air laden with bromine vapour into the well-stirred liquid, in the manner already described for ethylene (T., 1920, **117**, 359), absorption occurred with extreme rapidity. The operation was continued until the attainment of a permanent pale yellow tint. The volume of the reaction mixture was then noted, after which a small measured volume (5 or 10 c.c.) was withdrawn and diluted with water. The slight excess of bromine was removed by aspirating air through the solution, and the hydrobromic acid present was then determined by titration with standard silver nitrate solution, control experiments having indicated absence of hydrolysis of the dissolved bromohydrins under the conditions adopted. The total amount of bromine passed into the liquid was determined by weighing the receptacle containing this reagent before and after the operation. The two values obtained as stated were utilised to calculate the distribution of bromine in the reaction; the amounts of bromine used stood in satisfactory agreement with the corresponding weights of allyl alcohol, when pure anhydrous preparations were used.

Further successive portions of allyl alcohol were then introduced into the reaction vessel, the various determinations being repeated on each occasion. The appended table contains a summary of the results obtained in one such series of experiments. The calculations take into account the changes of volume which occurred throughout the process, but no correction is made for the very slight loss of bromine by diffusion. The temperature of the solution varied from 1·5° to 3·5°, and the operations were conducted in diffused daylight.

Towards the end of the third stage a second phase appeared, and from this point onwards the lower layer, which consisted mainly of β-dibromohydrin, gradually increased in bulk.

Stage.	Total bromine present (grams).	Total bromine present as $C_3H_5(OH)_2Br$ + HBr (grams).	Percentage of total bromine reacting to form $C_3H_5(OH)_2Br$ + HBr.	Concentration of $C_3H_5(OH)_2Br$. Grams per litre.	Normality.
1	23·5	20·38	86·7	32·4	0·209
2	45·5	38·16	83·9	58·8	0·379
3	67·5	53·48	79·2	81·1	0·523
4	89·5	68·54	76·6	103·9	0·670
5	111·7	81·82	73·2	123·0	0·794
6	133·7	94·38	70·6	140·8	0·908
7	156·2	107·14	68·6	157·5	1·016

From these results it is evident that the mobile equilibrium already referred to suffers displacement towards the left as the reaction progresses and the products accumulate in the solution. The monobromohydrin : dibromohydrin ratio thus declines from 6·5 : 1 at the beginning of the series to 2·2 : 1 at the end. As in the case of ethylene, this result is probably due in part to the *difference in solubility* between the *monobromohydrin and* the dibromohydrin; the concentration of the latter product in the solution is thus kept relatively low by its separation as a distinct phase during the early part of the reaction, whilst the concentration of the monobromohydrin increases throughout a considerably longer period.

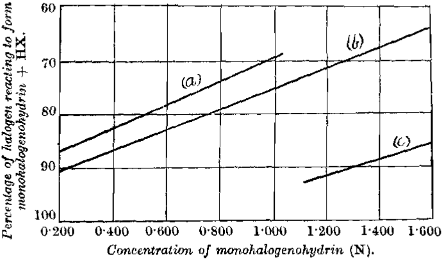
When the concentrations of monobromohydrin, as expressed by the *normality factor* (x), are plotted *against* the corresponding percentages of bromine functioning as hypobromous and hydrobromic acids (y), a regular curve is obtained [Fig. 1 (*a*)]; this approximates to a straight line, and is closely defined by the equation : $y = 91{\cdot}5 - 22{\cdot}9\,x$. The diagram (Fig. 1) illustrates the essential similarity of the reactions between (*a*) bromine water and allyl alcohol, (*b*) bromine water and ethylene (T., 1920, **117**, 1219), and (*c*) chlorine water and ethylene (Gomberg, *J. Amer. Chem. Soc.*, 1919, **41**, 1420). It is interesting to note that the halogenohydrin : dihalogenide ratio at corresponding concentrations increases from (*a*) to (*c*).

β-*Monobromohydrin*, $OH{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2{\cdot}OH$.—For the preparation of β-monobromohydrin, the reaction just described may conveniently be prolonged until the concentration of this substance in the solution has reached 1·0*N* to 1·25*N*, as disclosed by titration. The amount of monobromohydrin thus produced accordingly reaches about 60 per cent. of the theoretical yield. Although formed readily and in very satisfactory yield by this

thod, the isolation of the monobromohydrin from the aqueous uid and its subsequent separation from the accompanying bromohydrin in a state of purity presented appreciable difficulty. is result was due mainly to the instability of the monobromodrin when distilled repeatedly under diminished pressure; it ıst also be attributed partly to incomplete extraction of the bstance from the original aqueous solution.

The extraction was in all cases accomplished after careful neutralition of the ice-cooled solution with powdered sodium carbonate. ıirly satisfactory results were achieved by a threefold extraction ith ether after saturation with sodium chloride, or, better, with ıhydrous sodium sulphate, at the ordinary temperature. A milar extraction with acetone after saturation with calcium

FIG. 1.



chloride gave a somewhat higher yield. The best result was reached by saturating the solution with anhydrous sodium sulphate at 30° and extracting it with three successive quantities of ether; in this way the extraction attained an efficiency of about 70 per cent.

The ether extract, when dried over sodium sulphate and distilled from the water-bath, left a pale brown oil consisting of a mixture of the mono- and di-bromohydrins. The composition of this and all other similar mixtures examined in the course of the investigation was ascertained by alkaline hydrolysis, followed by a volumetric determination of bromide in the product. Control experiments demonstrated that mono- and di-bromohydrins are quantitatively hydrolysed when boiled for two hours under reflux with excess of aqueous potassium hydroxide.

In a particular preparation, the oily residue obtained from the ether extract, after being freed from ether by the passage of a rapid current of air, contained 61·2 per cent. of bromine. This result

corresponded with a mixture of 56·0 per cent. of monobromohydrin (Br = 51·6 per cent.) and 44·0 per cent. of dibromohydrin (Br = 73·4 per cent.). According to the titration of the original aqueous solution, 62 per cent. of the bromine had reacted to form monobromohydrin and hydrogen bromide; it follows, therefore, that the extraction of the dibromohydrin was somewhat more efficient than that of the more soluble monobromohydrin.

In all, 510 grams of oil were prepared, having characteristics agreeing closely with those of the preparation to which reference has just been made. The isolation of the two constituents was accomplished by continued fractional distillation under a pressure of about 20 mm. The oil, which was neutral to litmus, was distilled in portions from a Claisen flask fitted with a short fractionating column and heated by means of an oil-bath. The progress of the separation was followed by means of the bromine values of the fractions, corrections being applied, when necessary, for small amounts of hydrogen bromide formed during the process. It was found that the monobromohydrin, which is the constituent of higher boiling point, underwent a slow polymerisation, or analogous change, during the distillation. Consequently, after the six distillations which were undertaken in the attempt to prepare chemically pure products, only a small quantity of the monobromohydrin was obtained, the bulk of the substance having been transformed partly into a less volatile liquid, distilling over an indefinite range of temperature, and partly into a thick black tar. By curtailing the number of distillations, a much higher yield of only slightly impure β-monobromohydrin could be secured.

The following table, in which are embodied the results of the third fractional distillation of the above series, indicates the way in which the separation proceeds:

Fraction.	Range of fraction.	Weight of fraction (grams).	Percentage of combined bromine.	Percentage of $C_3H_5(OH)_2Br$.	Percentage of $C_3H_5(OH)Br_2$.
1	90—112°	15·5	41·5	—	—
2	112—116	82·0	71·9	7·0	93·0
3	116—118	143·3	70·8	11·8	88·2
4	118—125	43·0	69·9	16·0	84·0
5	125—135	32·3	62·6	49·4	50·6
6	135—140	17·5	56·7	76·7	23·3
7	140—143	23·1	51·1	100	—

Residue and loss during distillation, 65·8 grams.

During the course of the distillations it was noticed that fractions of fairly constant boiling point, and giving analytical results corresponding closely with (*a*) monobromohydrin, and (*b*) dibromohydrin, respectively, tended to distil in the neighbourhood of

140°/20 mm., and (*b*) 110°/20 mm. The two kinds of fractions icated were accumulated until the end of the fifth fractionation, ɔn it appeared of little use to prolong the process. Accordingly, h of the fractions in question was submitted to a final fractiona- ı. The monobromohydrin fraction, which weighed 55 grams, ɪrly all distilled at 136—138°/21 mm., and on alkaline hydrolysis re 51·6 per cent. of bromine ($C_3H_7O_2Br$ requires Br = 51·6 per ɪt.). It was thus regarded as chemically pure β-monobromo- drin. The dibromohydrin fraction, which weighed 210 grams, tilled completely at 111—114°/20 mm., and contained 72·8 per ɪt. of bromine ($C_3H_6OBr_2$ requires Br = 73·4 per cent.). Thus, the dibromohydrin present in the original 510 grams of crude oduct, about 90 per cent. was isolated in a state of purity; whilst the monobromohydrin not quite 20 per cent. was isolated.

The β-monobromohydrin thus obtained was a colourless and very scous liquid. On keeping for some time, it developed a pale ɛllow colour. Its vapour had an irritant action similar to that of hylenebromohydrin (T., 1920, **117**, 1221). It was miscible with cohol, acetone, or ether, but only partly miscible with benzene at ıe ordinary temperature. A determination of density gave $^{20°}_{4°}$ 1·7858 (vacuum). It is of interest that the calculated ratio f its molecular radius to that of water (Holmes, T., 1913, **103**, 147) is 1·69. β-Monobromohydrin thus occupies a position etween nicotine (1·65) and phenol (1·70) in Holmes's table (*loc. cit.*,). 2164); like β-monochlorohydrin (*v. infra*), it thus appears to tand on the border line between miscible and partly miscible iquids. When gradually diluted with water at the ordinary emperature, complete miscibility occurred over a certain range; urther dilution produced a turbidity which persisted until a elatively large volume of water had been added.

β-*Dibromohydrin*, $CH_2Br\cdot CHBr\cdot CH_2\cdot OH$.—As already indicated, the foregoing method, although designed primarily for the production of β-monobromohydrin, led simultaneously to the isolation of comparatively large amounts of β-dibromohydrin. Further investigations were carried out with the object of modifying the method so as to promote the formation of dibromohydrin and to facilitate its separation from the reaction mixture. In accordance with these aims, the proportion of water used in the preparation was considerably reduced.

A solution of allyl alcohol in its own weight of water was cooled by immersion in melting ice and vigorously stirred. Liquid bromine was then added slowly from a burette. Rapid reaction occurred, and a heavy oily phase soon separated. At the end of the addition, the mixture was neutralised in the cold with powdered sodium

carbonate, and then saturated at the ordinary temperature with anhydrous sodium sulphate. The oily layer was then separated and dried with the same agent. Mixed preparations made in this way, amounting to 350 grams, contained 67·5 per cent. of bromine. Since there was no evidence of subsidiary reactions having taken place, this result indicated the presence of 72·9 per cent. of dibromohydrin and 27·1 per cent. of monobromohydrin in the oil. The weight of oil isolated in this very simple way was about 88 per cent. of the calculated amount. The extraction was therefore decidedly more efficient than in the preceding method, whilst the proportion of dibromohydrin in the mixture was almost double the former amount. It may be added that this ratio was confirmed by titrimetric estimations of the hydrogen bromide produced in the reaction, the percentage of bromine reacting to form dibromohydrin in two such experiments being 70·7 and 74·1, respectively.

Purification of the dibromohydrin was effected by repeated fractional distillation from a Claisen flask provided with a short fractionating column, the process being controlled by observation of boiling points and analysis of the fractions, in the manner already described. After three fractionations, a yield of 223 grams of dibromohydrin was obtained, boiling at 111—114°/20 mm., and giving 72·1 per cent. of bromine on alkaline hydrolysis ($C_3H_6OBr_2$ requires Br = 73·4 per cent.). The preparation was therefore not quite as pure as the first one described, which had been fractionally distilled six times. The above yield amounts to 87 per cent. of the dibromohydrin present in the crude oil; when referred to the weight of allyl alcohol used, it corresponds with about 50 per cent. of the weight of dibromohydrin theoretically possible.

β-Dibromohydrin is a heavy liquid with an irritating odour. It is less viscous than β-monobromohydrin, and it remains colourless when kept. It is miscible with ether, alcohol, or acetone, and also with benzene; in the last respect it differs from β-monobromohydrin. It is only slightly soluble in water at the ordinary temperature. The density of the purer specimen noted above (Br = 72·8 per cent.) was determined as $d_{4^\circ}^{20^\circ}$ 2·1197 (vacuum); the Holmes value is thus 1·79. The second preparation described (Br = 72·1 per cent.) gave $d_{4^\circ}^{20^\circ}$ 2·1019. A specimen of Kahlbaum's β-dibromohydrin contained only 70·2 per cent. of bromine, and had $d_{4^\circ}^{20^\circ}$ 2·0897.

The Reaction between Allyl Alcohol and Chlorine Water.

A preliminary control experiment showed that when chlorine is passed into ice-cooled water in diffused daylight the amount of hydrochloric acid produced is so small as to be negligible in titrimetric estimations of the kind described in this paper. Accordingly,

ction of cold dilute chlorine water on allyl alcohol was studied e manner adopted for bromine water, the allyl alcohol being d in seven or eight portions of about 10 grams to a volume of r originally measuring 600 c.c. Very ready reaction ensued, the results of the quantitative estimations failed to exhibit the ced regularity observed in the case of bromine. The following mary indicates that the apparent monochlorohydrin : dichloro-in ratio fluctuated somewhat at the beginning of the reaction then declined very slowly. Owing to the vigour of the reaction emed likely that these results were influenced considerably by occurrence of subsidiary reactions; this inference was borne by an analysis of the quantitative data obtained in several es of experiments.

ge.	Percentage of total chlorine reacting to form $C_3H_5(OH)_2Cl$ + HCl.	Normality of $C_3H_5(OH)_2Cl$.	Stage.	Percentage of total chlorine reacting to form $C_3H_5(OH)_2Cl$ + HCl.	Normality of $C_3H_5(OH)_2Cl$.
1	78·4	0·189	5	75·3	0·953
2	81·4	0·361	6	74·5	1·088
3	79·4	0·528	7	74·9	1·208
4	79·1	0·678			

With 50 per cent. aqueous solutions of allyl alcohol, reaction urred so vigorously that even with very efficient cooling and rring it was found necessary to pass the chlorine very slowly and dilute it with air. During the process the liquid became yellow d formed two liquid phases, but these usually reverted to a mogeneous solution on completion of the reaction. The various eparations, made in the two ways indicated, when united amounted 594 grams; the product contained 35·05 per cent. of chlorine, as own by alkaline hydrolysis, and hence the apparent proportion monochlorohydrin present was 87·1 per cent. After a series of ght systematic fractional distillations under diminished pressure, nducted and controlled in the manner already explained for the rresponding bromine derivatives, it appeared that the mixture ntained, not only the two chlorohydrins anticipated, but also ppreciable quantities of materials of lower and higher boiling oints. The characteristics of the main fractions ultimately btained are summarised in the appended table:

Fraction.	Boiling point.	Pressure (mm.).	Weight of fraction (grams).	Percentage of chlorine.
1	81—81·5°	13·5	104·3	52·6
2	122·5—123·5	13·5	86·4	31·6
3	125—198	13·5	59·3	33·3

($C_3H_6OCl_2$ requires Cl = 55·0; $C_3H_7O_2Cl$ requires Cl = 32·1 per cent.).

In accordance with their constant boiling points and general properties, fractions 1 and 2 were regarded as consisting of β-dichloro- and β-monochloro-hydrin, respectively, although it is to be noted that the chlorine value, determined by hydrolysis with aqueous alkali, was somewhat low in the former instance. Alkaline hydrolysis in alcoholic solution gave an almost identical result, which was also confirmed by the method of Carius. The yields of dichlorohydrin calculated on the weights of (*a*) allyl alcohol, and (*b*) crude oil are (*a*) 11·2 and (*b*) 17·6 per cent., respectively. The corresponding yields of monochlorohydrin are (*a*) 10·8 and (*b*) 14·5 per cent. The united yields of monochlorohydrin and dichlorohydrin are, therefore, (*a*) 22·0 and (*b*) 32·1 per cent.

It is thus apparent that although the action of chlorine water on allyl alcohol leads to the production of β-monochlorohydrin and β-dichlorohydrin, the yields of these two substances are low and their separation in a state of purity is difficult. This result must be attributed in large measure to the vigour of the reaction, which entails the conversion of a high proportion of the allyl alcohol into other products.

β-Monochlorohydrin, $OH\cdot CH_2\cdot CHCl\cdot CH_2\cdot OH$. — β-Monochlorohydrin, prepared in the manner just described, was a colourless and very viscous liquid, possessing a marked irritating odour and boiling at 122·5—123·5°/13·5 mm. When kept for some time it became pale yellow. It was miscible with alcohol, ether, or acetone, but only partly miscible with benzene. Determinations of density gave $d_{4^\circ}^{0^\circ}$ 1·3416 and $d_{4^\circ}^{20^\circ}$ 1·3241 (vacuum). The ratio of the molecular radius to that of water is thus 1·67. When diluted with water at the ordinary temperature, β-monochlorohydrin behaved similarly to β-monobromohydrin. It is to be noted that the observations now recorded differ from the statements of other investigators to the effect that β-monochlorohydrin and β-monobromohydrin are completely miscible with water (compare Henry, *loc. cit.*, and Biilmann, *loc. cit.*). In the case of ethylenebromohydrin the difficulty of eliminating the last traces of the non-miscible dibromide was described in a former paper (*loc. cit.*, p. 1216); but although similar difficulties exist in these instances, the monohalogenohydrins clearly approach the region of partial miscibility in Holmes's table. The glyceryl monobromohydrin described by Veley (*Jahresber.*, 1883, 858) is stated to be immiscible with water (b. p. 160°/60 mm., $d_{4^\circ}^{4^\circ}$ 1·717), whilst the supposed glyceryl monobromohydrin of Wohl and Neuberg, obtained in small yield by the action of calcium hypobromite and boric acid on allyl alcohol (*Ber.*, 1899, **32**, 3490), was crystallised from aqueous solution (m. p. 227—230°).

fraction 3 in the above table, boiling indefinitely at 125—198°/5 mm., possessed similar solubility relationships, but its density s appreciably higher: $d_{4^\circ}^{0^\circ}$ 1·3571; $d_{4^\circ}^{20^\circ}$ 1·3382 (vacuum). The ction would thus appear to contain an isomeric monochlorodrin, and in mentioning this possibility attention may be directed the reported occurrence of several unexpected isomeric mono-omohydrins, including the curious solid compound prepared by ohl and Neuberg (*loc. cit.*).

β-*Dichlorohydrin*, $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OH$.—The specimen of lichlorohydrin described above was colourless and less viscid than monochlorohydrin, and it developed no yellow colour on keeping. distilled very regularly at 81—81·5°/13·5 mm. It was miscible ith alcohol, ether, or acetone, and also with benzene, but was ly slightly soluble in water at the ordinary temperature. Two terminations of density were made: $d_{4^\circ}^{0^\circ}$ 1·3745; $d_{4^\circ}^{20^\circ}$ 1·3534 acuum). The Holmes ratio, calculated from the latter value, is 74.

Summary.

1. Cold chlorine water and bromine water have been shown to act with allyl alcohol to produce in each instance glyceryl β-ionohalogeno- and β-dihalogeno-hydrin, the former in pre-ominating amount.

2. With chlorine water, the process is difficult to control, and much of the allyl alcohol is converted to other products; but with romine water the reaction pursues a course parallel to that between romine water and ethylene, and should be of practical importance s a preparative method.

3. The physical characteristics of the four halogenohydrins thus prepared are summarised in the following table and compared with he corresponding data available for other preparations of these ubstances:

	Boiling point.		$d_{4^\circ}^{t^\circ}$.	
Substance.	Observed.	Recorded.	Observed.	Recorded.
β-Monochloro-hydrin	122·5—123·5°/13·5 mm.	146°/18 mm. (Hanriot)	d^{0° 1·3416 d^{20° 1·3241	d^{0° 1·328 (Hanriot)
β-Dichloro-hydrin	81—81·5°/13·5 mm.	182°/1 atm. (Tollens)	d^{0° 1·3745 d^{20° 1·3534	d^{0° 1·3799 (Tollens)
β-Monobromo-hydrin	136—138°/21 mm.	138°/17 mm. (Fink)	d^{20° 1·7858	—
β-Dibromo-hydrin	111—114°/20 mm.	115—120°/18 mm. (Kohler) 100°/10 mm. (Forster and Withers)	d^{20° 2·1197	d^{25° 2·1259 (Philip) d^{0° 2·148 (Pariselle *)

* *Ann. Chim.*, 1911, [viii], **24**, 387.

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CXVIII.—*Studies in the Dihydronaphthalene Series. Part III. The Oxidation and Bromination of 5 : 8-Dihydro-α-naphthylamine.*

By Frederick Maurice Rowe and John Stanley Herbert Davies.

It has been shown previously that *ar*-tetrahydro-α-naphthylamine possesses many interesting properties, for in some cases it exhibits the properties of a benzenoid amine in which the hydrogenated ring may be regarded as a side-chain, whereas in other respects it retains the characteristics of a naphthalenoid amine.

The experiments carried out by one of us on the hydrogenation of α-naphthylamine (T., 1918, **113**, 955; *J. Soc. Dyers and Col.*, 1919, **35**, 128; *J. Soc. Chem. Ind.*, 1920, **39**, 241T; T., 1920, **117**, 1574) have indicated that there is a definite gradation in certain properties in the scheme of α-naphthylamine, 5 : 8-dihydro-α-naphthylamine, 7 : 8- or 5 : 6-dihydro-α-naphthylamine, to *ar*-tetrahydro-α-naphthylamine.

In this connexion, it appeared of interest, therefore, to examine the behaviour of the dihydro-α-naphthylamines when submitted to other reactions, such as oxidation and bromination, in order to determine whether in such cases also these compounds exhibit properties intermediate between those of α-naphthylamine and *ar*-tetrahydro-α-naphthylamine.

A.—*The Oxidation of 5 : 8-Dihydro-α-naphthylamine.*

When 1 : 4-dihydronaphthalene and 1 : 2-dihydronaphthalene are oxidised with alkaline permanganate the hydrogenated ring is opened at the double linking with the formation of *o*-phenylenediacetic acid and *o*-carboxy-β-phenylpropionic acid respectively. The fact that the latter compound is also formed by the oxidation of tetrahydronaphthalene indicates that in this case the hydrogenated ring behaves as a side-chain of the benzenoid ring. The nature of a substituent group in one ring of the naphthalene molecule, as is well known, determines which of the two rings will be affected by oxidation, thus α-nitronaphthalene yields nitrophthalic acid, whereas α-naphthylamine yields phthalic acid. In the case of *ac*-tetrahydro-α- or -β-naphthylamine, however, the introduction of four hydrogen atoms in the ring containing the amino-group affects the stability of the nucleus to such an extent that it is merely opened by oxidation by alkaline permanganate with the formation of *o*-carboxy-β-phenylpropionic acid in the place of phthalic acid. In the case of *ar*-tetrahydro-α- or -β-naphthylamine,

on the other hand, complete disruption of the ring containing the amino-group occurs, but the oxidation proceeds past the stage of a cyclic dicarboxylic acid, and the second nucleus is opened at the double linking with the formation of adipic acid.

In view of these considerations, it was probable that both rings in the dihydro-α-naphthylamines would be unstable to oxidation with alkaline permanganate, the hydrogenated ring because it is definitely unsaturated, and the other because it contains an amino-group. Even if βγ-dihydromuconic acid were formed as the first stage in the oxidation of 5 : 8-dihydro-α-naphthylamine, it was improbable that this compound could be isolated, as it was shown by Rupe (*Annalen*, 1889, **256**, 12) that it is converted into a mixture of malonic and oxalic acids by alkaline permanganate. When 5 : 8-dihydro-α-naphthylamine was oxidised with alkaline permanganate, oxalic acid was the only oxidation product which could be isolated, and although the conditions of the oxidation were varied with regard to the temperature, duration of the reaction, and the amount of permanganate used, oxalic acid was the only oxidation product, together with unaltered 5 : 8-dihydro-α-naphthylamine in some cases.

It was shown by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1124) that *ar*-tetrahydro-α-naphthylamine is oxidised to *ar*-tetrahydro-α-naphthaquinone by treatment with acid dichromate, but it was difficult to predict whether the oxidation of the isomeric dihydro-α-naphthylamines under similar conditions would result in the formation of dihydro-α-naphthaquinones, or whether the oxidation would proceed further. Actually the latter proved to be the case, for the main product of the oxidation of 5 : 8-dihydro-α-naphthylamine was α-naphthaquinone, together with a small proportion of phthalic acid, and although the oxidation was repeated under a variety of conditions, no dihydro-α-naphthaquinone could be isolated. The oxidation of 7 : 8- or 5 : 6-dihydro-α-naphthylamine also resulted in the formation of α-naphthaquinone, together with a small proportion of phthalic acid.

A somewhat similar result was observed by Bamberger and Kitschelt (*Ber.*, 1890, **23**, 876), who found that a mixture of α-naphthaquinone and α-naphthol was formed by the oxidation of *ac*-tetrahydro-β-naphthylamine with acid dichromate.

B.—*The Bromination of* 5 : 8-*Dihydroaceto-α-naphthalide and of* 5 : 8-*Dihydro-α-naphthylamine.*

It has been shown by Morgan, Micklethwait, and Winfield (T., 1904, **85**, 736) that when *ar*-tetrahydroaceto-α-naphthalide is treated with a solution of bromine in chloroform, an intermediate

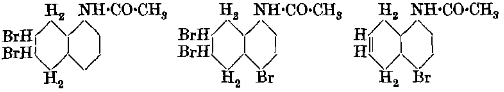
bromoamine is formed which is subsequently converted into 4-bromo-*ar*-tetrahydroaceto-α-naphthalide. A study of 4-bromo- and 4-sulpho-*ar*-tetrahydro-α-naphthylamine led these authors to the conclusion that the reactivity of the hydrogen atom in the ortho-position with respect to the amino-group is a characteristic property of the naphthalene molecule which is destroyed when the non-substituted ring undergoes hydrogenation.

In the case of β-naphthylamine, Smith (T., 1904, **85**, 728) found that the hydrogen atom in the 1-position, which readily undergoes substitution in β-naphthylamine, has to a great extent lost its reactivity in *ar*-tetrahydro-β-naphthylamine, and is comparable with the hydrogen in the ortho-position with respect to the amino-group in a benzenoid amine. Thus, the bromination of *ar*-tetrahydroaceto-β-naphthalide gives rise to 4-bromo- and 1-bromo-*ar*-tetrahydroaceto-β-naphthalide, whereas, under similar conditions, aceto-β-naphthalide yields only 1-bromoaceto-β-naphthalide. The decreased reactivity of the hydrogen atom in the 1-position in *ar*-tetrahydro-β-naphthylamine is exemplified further by the fact that treatment of this base with formaldehyde results in the formation of an anhydro-base analogous to methyleneaniline, and there is no tendency towards the production of an acridine (Smith, T., 1904, **85**, 732).

In comparison with these results, the bromination of 5 : 8-dihydro-α-naphthylamine is of interest on account of the variety of the products which is obtained, together with the fact that bromination is accompanied to a certain extent by dehydrogenation. The literature contains numerous examples of dehydrogenation in the benzene series effected by means of halogens, for example, Crossley and Haas (T., 1903, **83**, 495) found that 3 : 5-dichlorodihydrobenzene is converted into *m*-dichlorobenzene by treatment with phosphorus pentachloride or by the action of a solution of bromine in chloroform, whilst Zelinsky (*Ber.*, 1895, **28**, 782) showed that 1 : 3-dimethyl*cyclo*hexane yields tetrabromo-*m*-xylene on treatment with bromine and aluminium bromide. As far as the present authors are aware, however, no case of this nature has been recorded in which similar changes occur in the hydronaphthalene series.

When 5 : 8-dihydroaceto-α-naphthalide was treated with one molecular proportion of bromine in chloroform solution at 0°, the product consisted of a mixture of unaltered 5 : 8-dihydroaceto-α-naphthalide, 6 : 7-*dibromotetrahydroaceto-α-naphthalide* (I), and 4-bromoaceto-α-naphthalide. The yield of bromo-derivatives was low, however, so the proportion of bromine was increased to one and a half molecular proportions. In this case the main product of the reaction was 4 : 6 : 7-*tribromotetrahydroaceto-α-naphthalide*

(II), together with a small proportion of a *substance* melting at 187°, and some unaltered 5 : 8-dihydroaceto-α-naphthalide, but no 6 : 7-dibromotetrahydroaceto-α-naphthalide could be detected.



(I.) (II.) (III.)

6 : 7-Dibromotetrahydroaceto-α-naphthalide is converted into α-naphthylamine by treatment with methyl-alcoholic potassium hydroxide, and into 5 : 8-dihydroaceto-α-naphthalide by the action of zinc dust on a solution in methyl ethyl ketone, whilst 4 : 6 : 7-tribromotetrahydroaceto-α-naphthalide, when similarly treated, yields 4-bromoaceto-α-naphthalide and *4-bromo-5 : 8-dihydroaceto-α-naphthalide* (III), respectively.

Attempts to hydrolyse 6 : 7-dibromotetrahydroaceto-α-naphthalide and 4 : 6 : 7-tribromotetrahydroaceto-α-naphthalide with alcoholic potassium hydroxide or with sulphuric acid in order to obtain the free bases proved unsuccessful owing to the ease with which hydrogen bromide is removed from these compounds.

Consequently, an experiment was carried out in which 5 : 8-dihydro-α-naphthylamine was treated with one molecular proportion of bromine in chloroform solution at 0°. The product proved to be a complex mixture of amines, from which 2 : 4-dibromo-α-naphthylamine was isolated without great difficulty. Attempts to separate the residue into its constituents proved unsuccessful, however, until it was acetylated, after which a prolonged series of fractional crystallisations led to the isolation of 4 : 6 : 7-tribromotetrahydroaceto-α-naphthalide (II), 4-bromo-5 : 8-dihydroaceto-α-naphthalide (III), and 4-bromoaceto-α-naphthalide.

When 4-bromo-5 : 8-dihydroaceto-α-naphthalide was treated with dilute nitric acid, nitration and oxidation were simultaneously effected with the formation of 4-bromo-2-nitroaceto-α-naphthalide, identical with that obtained by the nitration of 4-bromoaceto-α-naphthalide (Liebermann, *Annalen,* 1876, **183**, 260, gives m. p. 232°).

The formation of some 4-bromo-5 : 8-dihydro-α-naphthylamine in the bromination of 5 : 8-dihydro-α-naphthylamine is of interest as showing that substitution by bromine occurs to a certain extent in preference to the saturation of the hydrogenated ring.

The behaviour of 7 : 8- or 5 : 6-dihydro-α-naphthylamine on bromination will be examined subsequently.

Experimental.

The 5 : 8-dihydro-α-naphthylamine and 7 : 8- or 5 : 6-dihydro-α-naphthylamine used in the following experiments were prepared as described by Rowe and Levin (T., 1920, **117**, 1574).

Oxidation of 5 : 8-*Dihydro-α-naphthylamine with Alkaline Permanganate*.—A number of oxidations were carried out under a variety of conditions, but as the main result was the same in all cases only one need be described. Ten grams of 5 : 8-dihydro-α-naphthylamine, 5—10 grams of sodium carbonate, and 200 c.c. of water were ground into a paste, cooled to 5°, and 1 litre of 4 per cent. aqueous potassium permanganate solution was added drop by drop with agitation at that temperature. When the oxidation was complete, the mixture was boiled and filtered. The residue was extracted with boiling water, and the combined filtrates and residue were extracted several times with ether. Unaltered 5 : 8-dihydro-α-naphthylamine was recovered from the ethereal extract in the form of its hydrochloride (4 grams). The examination of the aqueous filtrate was based on the fact that βγ-dihydromuconic acid and oxalic acid are very sparingly soluble in ether, whereas malonic acid is readily soluble in this solvent. The first two acids can be separated by taking advantage of the fact that calcium oxalate is soluble in hydrochloric acid, whereas βγ-dihydromuconic acid is precipitated by hydrochloric acid. The combined aqueous filtrates were concentrated under diminished pressure, acidified, and extracted with ether. The ether extract contained a little resinous matter, but no malonic acid. The aqueous solution was then neutralised with ammonia, precipitated with calcium nitrate, and filtered. Nothing further could be isolated from the filtrate. The white, amorphous precipitate (4 grams) was completely soluble in hydrochloric acid. The calcium was removed as sulphate, and pure oxalic acid was isolated from the filtrate.

Oxidation of 5 : 8-*Dihydro-α-naphthylamine with Acid Dichromate*.—A suspension of the finely divided sulphate was prepared from 9 grams of 5 : 8-dihydro-α-naphthylamine, 250 c.c. of water, and 75 grams of sulphuric acid, and an aqueous solution of 8 grams of potassium dichromate was added slowly below 10°. The mixture was kept over-night, and as it contained unchanged amine, a further quantity of dichromate was then added. When the oxidation was complete the mixture was filtered, and the precipitate and filtrate were extracted with ether. Phthalic acid was extracted from the residue with dilute sodium hydroxide. The ethereal extracts were distilled, and a residue of dark brown needles was obtained. This was purified by distillation in a current of steam

formed yellow needles of α-naphthaquinone melting at 124—

he oxidation of 7 : 8- or 5 : 6-dihydro-α-naphthylamine with dichromate similarly yielded only α-naphthaquinone and halic acid.

mination of 5 : 8-*Dihydroaceto-α-naphthalide with one Molecular Proportion of Bromine.*

solution of 9·4 grams of bromine in 90 c.c. of dry chloroform added drop by drop with agitation to a solution of 11 grams 5 : 8-dihydroaceto-α-naphthalide, m. p. 164°, in 100 c.c. of oroform at 0°. The solution was concentrated at the ordinary aperature until the separation of a white, crystalline precipitate s complete. The product proved to be a mixture, which was parated by repeated fractional crystallisation, using alcohol, etic acid, and solvent naphtha as solvents, into 6 : 7-*dibromo-rahydroaceto-α-naphthalide*, silky, feathery needles melting 179—179·5° (Found: C = 41·20; H = 3·76; Br = 46·11. $_{2}H_{13}ONBr_{2}$ requires C = 41·50; H = 3·75; Br = 46·11 per nt.), and 4-bromoaceto-α-naphthalide, flat, glistening needles elting at 193°. The melting point of the latter compound was ot depressed by admixture with 4-bromoaceto-α-naphthalide otained by brominating aceto-α-naphthalide (Meldola, *Ber.*, 1878, 1, 1906). The remainder of the chloroform solution yielded a sinous product, from which 5 : 8-dihydroaceto-α-naphthalide only as isolated with difficulty.

6 : 7-*Dibromotetrahydroaceto-α-naphthalide* is readily soluble in ot alcohol, acetic acid, toluene, benzene, and cold pyridine, but paringly soluble in hot light petroleum. When it is heated above ts melting point or when heated with sulphuric acid, hydrogen romide is evolved.

Conversion of 6 : 7-*Dibromotetrahydroaceto-α-naphthalide into α-Naphthylamine.*—A solution of 1 gram of 6 : 7-dibromotetra-ydroaceto-α-naphthalide and 5 grams of potassium hydroxide in 0 c.c. of methyl alcohol was boiled under reflux for one and a half hours. The potassium bromide which separated was filtered, and the filtrate diluted with water and extracted with ether. The ether was removed, and the residue crystallised from alcohol and identified as α-naphthylamine, colourless needles melting at 50°.

Conversion of 6 : 7-*Dibromotetrahydroaceto-α-naphthalide into* 5 : 8-*Dihydroaceto-α-naphthalide.*—An excess of zinc dust was added to a boiling solution of 1 gram of 6 : 7-dibromotetrahydroaceto-α-naphthalide in the minimum quantity of methyl ethyl ketone and the mixture boiled under reflux for one hour. The zinc was

removed and the filtrate evaporated to dryness. The residue was crystallised several times from solvent naphtha. The product was identified as 5 : 8-dihydroaceto-α-naphthalide, silky, felted needles melting at 164°.

Bromination of 5 : 8-*Dihydroaceto-α-naphthalide with one and a half Molecular Proportions of Bromine.*

The bromination was effected as already described except that an increased quantity of bromine was used. The yield of crystalline product was increased considerably, and after several crystallisations from glacial acetic acid, the main product proved to be 4 : 6 : 7-*tribromotetrahydroaceto-α-naphthalide*, well-defined, colourless needles melting at 201·5—202° (Found: C = 34·16; H = 2·95; Br = 56·16. $C_{12}H_{12}ONBr_3$ requires C = 33·80; H = 2·82; Br = 56·34 per cent.).

In addition, some unaltered 5 : 8-dihydroaceto-α-naphthalide was isolated, together with a small quantity of a *substance* which contained bromine and crystallised in colourless needles melting at 187°.

4 : 6 : 7-*Tribromotetrahydroaceto-α-naphthalide* is difficultly soluble in alcohol, slowly soluble in hot acetic acid, insoluble in ether, benzene, and toluene, moderately soluble in hot ethyl acetate, and readily soluble in hot solvent naphtha and in cold pyridine. When it is heated above its melting point, hydrogen bromide is evolved.

Conversion of 4 : 6 : 7-*Tribromotetrahydroaceto-α-naphthalide into* 4-*Bromoaceto-α-naphthalide.*—A solution of 1 gram of 4 : 6 : 7-tribromotetrahydroaceto-α-naphthalide and 4 grams of potassium hydroxide in 30 c.c. of methyl alcohol was boiled under reflux for two hours. The potassium bromide which separated was filtered, and the filtrate was precipitated with water and extracted with ether. The product, which was crystallised from alcohol and then from solvent naphtha, was identified as 4-bromoaceto-α-naphthalide, flat, silvery needles melting at 193°.

Conversion of 4 : 6 : 7-*Tribromotetrahydroaceto-α-naphthalide into* 4-*Bromo*-5 : 8-*dihydroaceto-α-naphthalide.*—This was effected in a similar manner to that already described for the conversion of 6 : 7-dibromotetrahydroaceto-α-naphthalide into 5 : 8-dihydroaceto-α-naphthalide. The product was crystallised from solvent naphtha and formed flat, silvery needles melting at 213·5° with previous softening (Found: C = 53·80; H = 4·56; Br = 30·25 $C_{12}H_{12}ONBr$ requires C = 54·13; H = 4·51; Br = 30·07 per cent.).

4-*Bromo*-5 : 8-*dihydroaceto-α-naphthalide* is readily soluble in hot alcohol, acetic acid, pyridine, acetone, and methyl ethyl ketone When it is heated with sulphuric acid, sulphur dioxide is evolved; an attempt to make use of this reaction for the oxidation of the dihydro-derivative to 4-bromoaceto-α-naphthalide failed.

Treatment of 4-Bromo-5 : 8-dihydroaceto-α-naphthalide with Dilute [Ni]tric Acid.—An excess of dilute nitric acid (1 part of nitric acid, [d] 1·42, to 4 parts of water) was added to a solution of 1 gram of [4-]bromo-5 : 8-dihydroaceto-α-naphthalide in glacial acetic acid, and [th]e mixture boiled for some time. After cooling and diluting with [w]ater, a yellow, crystalline precipitate separated, which was filtered, [an]d crystallised several times from dilute acetic acid. 4-Bromo-[?-]nitroaceto-α-naphthalide forms long, faintly coloured needles [m]elting at 234°.

Bromination of 5 : 8-Dihydro-α-naphthylamine with one Molecular Proportion of Bromine.

A chloroform solution of 22·6 grams of 5 : 8-dihydro-α-naphthyl[a]mine was treated with a chloroform solution of bromine (1 mol.) [i]n a similar manner to that already described for 5 : 8-dihydroaceto-[α]-naphthalide. When the chloroform solution was concentrated, [2]8·5 grams of a crystalline product were obtained, and the filtrate [c]ontained resinous by-products. The crystalline product proved to [b]e a mixture of amines, only one of which, 2 : 4-dibromo-α-naphthyl[a]mine, could be isolated after repeated crystallisation from dilute [a]lcohol. 2 : 4-Dibromo-α-naphthylamine forms almost colourless [n]eedles melting at 116·5° (Found: C = 39·62; H = 2·52; Br = 53·29. Calc., C = 39·87; H = 2·33; Br = 53·16 per cent.), and on acetylation yields 2 : 4-dibromoaceto-α-naphthalide melting at 226°. These products were identical with those described by Meldola (*Ber.*, 1879, **12**, 1961). In order to isolate the other products of bromination, the residue was crystallised several times from a mixture of toluene and alcohol at 85°. The crystalline product, flat needles or plates, which analysis showed to be a mixture, was then acetylated. After a prolonged series of fractional crystallisations, in which acetic acid, acetone, methyl ethyl ketone, and solvent naphtha were used as solvents, it was possible to isolate 4 : 6 : 7-tribromotetrahydroaceto-α-naphthalide, glistening needles melting at 201·5—202°, identical with that already described, 4-bromo-5 : 8-dihydroaceto-α-naphthalide, long, flat, glistening needles melting at 214° (Found: C = 53·76; H = 4·76; Br = 30·27 per cent.), identical with that already described, and 4-bromoaceto-α-naphthalide, needles, melting at 193°.

It is desired to acknowledge a grant made to one of us (J. S. H. D.) by the Department of Scientific and Industrial Research which has enabled this investigation to be carried out.

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CXIX.—*The Reactivity of Ammonia.*

By EDWARD CHARLES CYRIL BALY and HERBERT MAXWELL DUNCAN.

IN a recent paper (Baly and Barker, T., 1921, **119**, 653), some results were described which had been obtained during a quantitative investigation of the photochemical reaction between hydrogen and chlorine. It was found that on exposing the mixture of these two gases to light of various intensities the velocity of union during the first few minutes increases up to a maximum which remains constant. This result has such great significance in relation to modern views of chemical reaction that we undertook some experiments in order to see if a similar result could be obtained in analogous cases. The essential condition for the observation of the phenomenon is the stimulation of an exothermic reaction by the supply of energy at a constant rate, the phenomenon itself being due to the reabsorption by the surrounding molecules of the energy that is radiated during the reaction. A series of measurements was made of the decomposition of nitrous oxide by a platinum wire heated by a constant current. It is sufficient to record the fact that during the first few seconds the velocity of decomposition increases to a maximum, just as in the case of the union between hydrogen and chlorine. When ammonia was substituted for the nitrous oxide, this phenomenon was not observed, but this is to be expected, since the decomposition of ammonia is an endothermic reaction.

In the case of ammonia, the very remarkable fact was noticed that with the platinum wire heated at a constant temperature the amount of decomposition effected in a given time varied very considerably with the velocity with which the sample of gas had been withdrawn from a cylinder of the compressed gas. This phenomenon has been investigated by us in detail, and it is only after eighteen months' work, during which the most rigid tests have been applied, that we now lay our results before the Chemical Society.

The apparatus employed consisted simply of a wide glass tube closed at both ends, with a short piece of stout platinum wire sealed in at each end. A coil of thin platinum wire was attached to these two stout wires and this coil was heated by means of an electric current from accumulators. The glass vessel was provided with an entrance and an exit tube and was filled by passing a stream of ammonia through it. The vessel was completely immersed in a tank through which a constant stream of water was maintained. Since this water came direct from the low-level mains, no appre-

ciable variation in temperature took place during a day's work. The decomposition vessel was connected through a tube 0·5 mm. internal diameter and 1 metre long with a delicate manometer filled with xylene. The current was measured to within 0·01 ampere and the time was measured by a quarter-second clock.

The method of experimentation was as follows. The decomposition vessel, after being carefully cleaned and thoroughly dried, was filled with ammonia, and the internal pressure balanced against the atmosphere by means of the manometer. The vessel was then closed by stop-cocks on the entrance and exit tubes, and a known current was passed through the platinum wire for exactly ten or twenty seconds. After sufficient time had elapsed, connexion was remade with the manometer, and the expansion measured, the accuracy of measurement being 0·004 c.c. It is obvious from this method of experiment that any two observations could be made strictly comparable, since, if no change is made in the wire, the passage of the same amount of electricity through the wire for the same time causes a radiation of the same amount of energy to the ammonia in the vessel. This was experimentally confirmed, because with a constant current during a constant time the same sample of ammonia always was decomposed to the same extent, provided no change was made in the wire. For the sake of convenience a series of decompositions of ordinary ammonia was carried out with different currents, the time being the same in each, and from these a curve was drawn. The results obtained with any given current for the same time could at once be checked against this curve.

It has been proved conclusively that constant decomposition values are given by ammonia which has been obtained by slow escape from a cylinder of compressed gas or by gently heating the concentrated aqueous solution. It has also been proved that if the gas from either source is liquefied and allowed to evaporate isothermally at its boiling point, the ammonia thus obtained gives a decomposition value which is identical with that given by the two previous preparations of the gas. It has been previously mentioned that if ammonia is allowed to escape very rapidly from a cylinder containing the liquefied gas, different decomposition values are obtained, these being in point of fact much smaller than those given by ordinary ammonia. It was eventually found that when liquefied ammonia is rapidly evaporated, the gas gives a much lower decomposition value than ordinary ammonia.

There is no doubt that this phenomenon is a specific property of the ammonia and that two different types of ammonia can be prepared, an active and an inactive phase. This conclusion has

been definitely established by the following experiments. In the first place, two samples of ammonia can be prepared, one being active and the other inactive. These may be passed alternately into the apparatus and supplied with the same quantity of energy, when high and low decomposition values are alternately obtained. In the second place, if the decomposition vessel is filled with inactive ammonia, and the wire heated at about 200°, the gas after a short time will become active and give a decomposition value which is equal to that of normal or active ammonia. Active ammonia is not affected by this treatment. In the third place, a cylinder full of liquefied ammonia may be taken and by rapid evaporation of the liquid the inactive gas may be obtained. When the cylinder is allowed to remain, the gas left in the cylinder slowly recovers its normal activity, the time for complete recovery depending on the size of the cylinder. With a 15 lb. cylinder, the recovery will be complete within twelve hours, but with a 100 lb. cylinder, the recovery will not be complete until twenty-four hours have elapsed.

We have thus proved that the inactive ammonia becomes normal when allowed to remain for some hours in contact with the liquefied gas, but that in the absence of the liquid it does not recover unless gently heated.

In the following table are given a few results selected at random from amongst the many hundred measurements that we have made.

Type of ammonia.	Current (amperes).	Time in secs.	Expansion in c.c.	Percentage amount decomposed.
Active	4·00	20	0·46	1·00
,,	4·10	,,	0·65	1·41
,,	4·25	,,	1·04	2·26
,,	4·35	,,	1·36	2·96
,,	4·50	,,	2·16	4·70
Inactive	4·00	,,	0·22	0·48
,,	4·10	,,	0·37	0·80
,,	4·25	,,	0·65	1·41
,,	4·35	,,	0·93	2·01
,,	4·50	,,	1·60	3·48

The difference between the results obtained with the active gas and the inactive gas is very clearly shown. By the measurement of the amount of decomposition when the same sample of ammonia is twice heated, using the same current for the same time in each case, further confirmatory evidence has been obtained, since the ratios between the first and second decompositions are markedly different with the two types of ammonia. In the case of active ammonia the ratio is about 2·6, whilst with the inactive ammonia the ratio is only about 1·5. It is evident from this that in the case of inactive ammonia part of the energy is utilised during the first heating in activating some of the inactive modification. It would

also seem to be established that the two types of ammonia, active and inactive, do not entirely consist of different phases, but that two different phases exist which require different amounts of energy to decompose them and that the active and inactive types *differ in the relative amounts of the two phases which they contain.* Whilst it is not possible from the measurements we have made to determine the relative amounts present, it appears to be established that the two phases exist, differing in their energy content.

We have also investigated the influence of water vapour on the decomposition of ammonia, and the results we have obtained are of particular interest in their bearing on H. B. Baker's well-known discovery that perfectly dry ammonia does not react with hydrogen chloride. We have found that the addition of water vapour to ammonia very greatly increases the amount of decomposition caused by a definite amount of energy, the increase depending on the amount of water vapour present. We have further proved that ammonia, the activity of which has been increased by the *addition of water vapour, loses this increased activity when dried* by means of quicklime. The amount, therefore, of the reactive phase present is increased when the ammonia is moist, and is decreased when the ammonia is dried. The suggestion may be made that the amount of the active phase present will still further be decreased by more complete drying, and that, when absolutely dry, ammonia will consist only of the inactive phase. This would offer an explanation of the fact that perfectly dry ammonia does not react with hydrogen chloride, this particular reactivity being a property of our active phase. We endeavoured to obtain the decomposition value of ammonia that had been dried by phosphoric oxide, but we found that the results were vitiated by the presence of volatile phosphorus compounds. It may also be recorded that the decomposition value of ammonia is increased by xylene vapour and other hydrocarbons, although to a less extent than by water vapour. This fact is of some interest, since it is known that such substances cause perfectly dry ammonia to react with hydrogen chloride.

In discussing these results, attention may be directed to the very remarkable differences which have been observed between the absorption spectra of certain substances in the vapour and liquid states. Many compounds, more particularly the nitrogen compounds such as aniline, pyridine, piperidine, etc., show entirely different absorption bands as liquid and vapour. Whatever explanation may be accepted of this, the fact remains that the liquid and gaseous molecules differ from one another. Since this phenomenon has been observed with so many nitrogen compounds, it probably

also exists in the case of the parent substance, ammonia, and therefore the inactive gas may be assumed to contain more than the normal number of the molecules characteristic of the liquefied gas. Reference may also be made to the fact that when strong sulphuric acid is added to liquefied ammonia no combination takes place between the two liquids, but as the liquid ammonia evaporates, the gas readily combines with the acid. This observation supports the conclusion that the liquid consists of that molecular phase which does not react with acid, and also the deduction that our inactive phase is identical with the non-reactive ammonia prepared by Baker.

It follows from this that the active and inactive forms of ammonia should show different absorption spectra, and we hope to investigate this point. For this purpose, a vacuum spectrograph is necessary, since the absorption band of ammonia lies in the very extreme ultra-violet. Reference may also be made to the conception of gasogen and liquidogen molecules advanced by Traube (*Ann. Physik*, 1902, [iv], **8**, 267). A very interesting result has also been noted by Woltereck (*Compt. rend.*, 1908, **147**, 460) as regards the temperature at which ammonia decomposes. Pure dry ammonia, when passed through a heated glass tube, is not decomposed below 620°, but in the presence of water vapour or organic matter the decomposition begins at a considerably lower temperature. This observation agrees in every way with the experimental results now recorded.

These results conform to the theory of molecular phases put forward by one of us (Baly, *Phil. Mag.*, 1920, [vi], **40**, 15), according to which a molecule, when freshly synthesised, is metastable and at once loses energy and passes into one of a number of possible phases. The energy is lost in terms of the molecular quantum of energy which is a fundamental unit characteristic of the molecule. Each consecutive phase differs in energy content by one molecular quantum and each phase is characterised by a specific reactivity and by an absorption band, the frequency of which is an exact integral multiple of the fundamental molecular frequency. It is possible to change the phase in which a molecule exists by supplying energy to it or by taking energy from it. There are three methods of supplying energy to a molecule and of changing its phase. The energy may be given by a material catalyst, or the molecule may be exposed to long-wave radiation (heat) or to short-wave radiation (light). The increase in reactivity that ensues is due to the change in phase which is produced. In the case of ammonia, the two phases clearly differ in energy content, since a greater amount of energy is required to decompose the inactive phase. They also

differ in reactivity, since the inactive phase is doubtless that phase which Baker found to be incapable of reacting with hydrogen chloride. We do not claim to have prepared either of the two phases in the pure state, but we claim that our results establish the existence of the two phases and explain the want of reactivity of dry ammonia. In view of the present results and the change of molecular phase obtained on drying, it may well be suggested that similar phase changes may be produced on drying other substances. For example, it is to be expected that, if completely dried, aniline, pyridine, and piperidine vapours will be found to consist of the same phase as the liquids.

Finally, we may record some observations on the behaviour of the platinum wire. In our early experiments, a wire was used which previously had been employed in a long series of measurements of the decomposition of nitrous oxide, and it was with this wire that the first observations of the ammonia phenomenon were made. This wire was accidentally fused, and on setting up another apparatus fitted with a piece of the same wire we found that no difference could be detected in the decomposition values of the two types of ammonia. Several kinds of wire were tried, but in each case the result was the same. We found that the wire must be activated in some way, and that this may be effected by alternately heating the wire to 500° and cooling it, this being done at short intervals for several hours. We found also that the wire may be activated in the same way as is necessary in the catalytic oxidation of ammonia in air to nitric acid. A mixture of ammonia and air was passed through the decomposition vessel and the wire was electrically heated to bright redness. After a short time, the electric current being constant, the temperature of the wire began to increase. The current was then decreased little by little, until finally it was found that the wire remained incandescent when the current was stopped. When the wire had been so treated and activated in either of the above ways, the two types of ammonia at once gave the different decomposition values recorded above. Although the wire never loses its activity entirely after it has once been activated, yet the activity falls to a smaller and constant value after long use. The full activity can at once be restored by heating the wire to bright redness for about twenty seconds. Further, a fully activated wire suffers a loss in activity on heating at about 250° for a short time. This peculiar behaviour of the wire led us to investigate most carefully the possibility of our results having been due to the poisoning of the wire, but the evidence we have gained very definitely negatives this possibility. This may be judged from the following summary of our results.

Summary.

1. The decomposition of ammonia by means of a hot platinum wire has been measured.

2. Two types of ammonia may be prepared, an inactive and an active modification, which are decomposed to different extents by the same quantity of energy.

3. The active form is obtained by slow withdrawal of ammonia from a cylinder containing the compressed gas, by warming the concentrated aqueous solution and drying the gas by quicklime, and by isothermal evaporation of the liquefied gas at its boiling point.

4. The inactive form is obtained by rapid evaporation of the liquefied gas.

5. The inactive gas slowly recovers its activity on remaining in contact with the liquefied gas. The same effect can be produced by gently warming the gas by means of a platinum wire heated at 200°.

6. Active and inactive ammonia passed alternately into the same decomposition vessel give with a fixed supply of energy high and low decomposition values.

7. When the same sample of ammonia is twice exposed to the heated wire, the ratios of the amounts decomposed in the two cases differ very materially with the two forms.

8. The addition of water vapour increases the reactivity of ammonia, the increase being proportional to the amount of water vapour present. The enhanced reactivity is removed on drying the gas with quicklime.

9. Two different molecular phases of ammonia exist which possess different reactivities and require different amounts of energy to decompose them. The active and inactive forms of ammonia now described differ in the relative amounts of these two phases which they contain.

10. There is little doubt that the phase of lower energy content is identical with that which is obtained when ammonia is completely freed from moisture and which does not combine with hydrogen chloride.

11. In order to observe these phenomena, the platinum wire must be activated in the same way as is customary in the Ostwald process for the catalytic oxidation of ammonia in air to nitric acid. Alternatively, the activation may be effected by rapidly heating and cooling the wire for several hours.

In conclusion, we tender our thanks to the Department of Scientific and Industrial Research for a grant to one of us (H. M. D.) which has enabled this investigation to be carried out.

THE UNIVERSITY,
LIVERPOOL. [*Received, April 22nd*, 1922.]

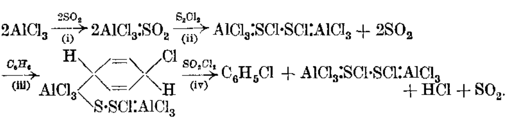
XX.—*Researches on Sulphuryl Chloride. Part II. A New Chlorinating Agent: Preparation of Polychloro-derivatives of Benzene.*

By OSWALD SILBERRAD.

THE new reagent consists essentially of a solution of sulphur monochloride in sulphuryl chloride, which, when brought into contact with aluminium chloride, gives rise to an aluminium sulphur chloride having the composition $Al_2S_2Cl_8$; this compound, in the presence of sulphuryl chloride, possesses the most remarkable chlorinating properties. In practice, it is not necessary to isolate the aluminium sulphur chloride; indeed, chlorination by its aid is most easily effected by allowing the solution of sulphur chloride in sulphuryl chloride to act on the compound to be chlorinated in the presence of aluminium chloride. In this manner, any degree of chlorination can be brought about. Thus chlorobenzene is readily converted into di-, tetra-, or hexa-chlorobenzene, according to the amount of sulphuryl chloride added, the operation being conveniently carried out on an ordinary water-bath. The activity of this reagent is the more remarkable when it is remembered that benzene may be boiled with pure sulphuryl chloride almost indefinitely without any appreciable quantity even of monochlorobenzene being produced (compare Dubois, *Z. Chem.* von Beilstein and Fritz Hübner, 1866, **2**, 705; Töhl and Eberhard, *Ber.*, 1893, **26**, 2941). The reactions involved appear to be rather complex; in the first place aluminium chloride dissolves in excess of sulphuryl chloride with evolution of chlorine and formation of the compound $AlCl_3{:}SO_2$, for which the name aluminium chlorosulphoxide is suggested (compare Adrianowsky, *Ber.*, 1879, **12**, 688; Ruff, *Ber.*, 1902, **35**, 4453). On adding sulphur to this solution, Ruff (*Ber.*, 1901, **34**, 1749) obtained sulphur mono-, di-, or tetra-chloride according to the temperature to which the reacting materials were allowed to rise. If, however, sulphur or sulphur monochloride be brought into contact with a fairly concentrated solution of the aluminium chlorosulphoxide, a thick, almost colourless crystalline magma possessing the composition Al_2Cl_6,S_2Cl_2 separates.* This

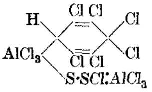
* It is interesting to note that, so far back as 1867, Baudrimot observed that "sheet aluminium reacts violently on gently warming with sulphur monochloride, a brown liquid distils over, and crystals, perhaps of a compound of aluminium chloride and sulphur chloride, are formed" (*Compt. rend.*, 1867, **64**, 368; *Jahresber.*, von Leibig and Kopp, 1867, 159). Until now, however, no one appears to have isolated this compound in a state of purity, or to have ascertained its composition. In this connexion, it should also be observed that under the conditions described above, no evidence was

compound is remarkably stable, and may be recrystallised from boiling thionyl chloride or sulphuryl chloride; in the latter case, however, considerable decomposition of the solvent occurs; but the chief peculiarity of this latter solution lies in its remarkable chlorinating properties. Thus, if a crystal of frozen benzene be added, chlorination occurs with almost explosive violence, and even such an inert substance as tetrachlorobenzene is readily converted into the hexachloro-derivative. It would appear that the remarkable activity of this reagent depends on the following series of reactions :

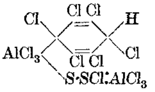


The reactions indicated by (iii) and (iv) appear to proceed continuously until either the sulphuryl chloride is expended or the hydrocarbon is completely chlorinated.

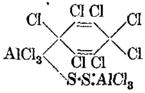
In studying these reactions, the formation of intense colours was observed in all cases so long as an unsubstituted group remained; the colour seems to disappear, however, as soon as substitution is complete. It would seem probable, therefore, that the deep moss-green compound to which pentachlorobenzene gives rise should be formulated as represented by I below, rather than by II, otherwise the compound represented by formula III should also be produced and possess chromophoric properties, which is contrary to experience :



(I.)



(II.)



(III.)

Such compounds, it will be observed, are strictly analogous to the substituted benzenoid chlorides described by Jungfleisch (*Z. Chem.* von Beilstein and Fritz Hübner, 1868, 4, 468), Willgerodt (*J. pr. Chem.*, 1897, [ii], **55**, 416), Otto (*Annalen*, 1867, **141**, 101), Matthews (*T.*, 1892, **61**, 104), and Barrals (*Bull. Soc. chim.*, 1895, [iii], **13**, 418), some of which, indeed, have been observed to form intensely

obtained of the formation of the unstable compound possessing the approximate composition corresponding with the formula $AlCl_3,SCl_4$ described by Ruff and Plato (*Ber.*, 1901, **34**, 1755).

oloured derivatives with great ease (compare Barral, *ibid.*, 1897, ii], **17**, 774). The action of this reagent on other hydrocarbons being studied, and particularly with a view to obtain new chlorides f carbon.

EXPERIMENTAL.

Examination of Intermediate Compounds.

(1) *Aluminium Chlorosulphoxide*, $AlCl_3{:}SO_2$.—This compound is best prepared by adding recently sublimed and finely ground anhydrous aluminium chloride (15 grams) to sulphuryl chloride (30 c.c.) and agitating the mixture until solution is complete—this occupies about eight hours, during which time the temperature should be allowed to rise gradually from 0° to 30° and moisture be rigidly excluded. The product is then filtered through a warm, dry filter-paper in a completely enclosed funnel, whereby a ruddy brown, flocculent substance, which contains the iron originally present in the aluminium chloride, is removed.

The solution of this substance obtained in this manner fumes strongly in the air, coats everything with which it comes into contact with a white, scaly layer, and possesses an odour reminiscent of phosphorus pentachloride; it is decomposed by water with a hissing sound, and reacts vigorously with benzene or similar hydrocarbons, producing highly chlorinated derivatives.

A small quantity of the solution was run into a weighed bulb, freed from excess of sulphuryl chloride by warming at 30° in a vacuum until constant in weight, and analysed (Found: Al = 13·56; Cl = 53·73. $AlCl_3{:}SO_2$ requires Al = 13·71; Cl = 53·85 per cent.).

(2) *Aluminium Sulphur Chloride*, $Al_2S_2Cl_8$ or $AlCl_3{:}SCl{\cdot}SCl{:}AlCl_3$, separates as a solid mass when sulphur monochloride or finely ground sulphur is added to the above solution of aluminium chlorosulphoxide; it is, however, best prepared by adding 5 grams of sulphur monochloride, previously dissolved in 45 c.c. of thionyl chloride, to a solution of the aluminium chlorosulphoxide in sulphuryl chloride prepared as above described from 10 grams of aluminium chloride. On mixing these solutions at the ordinary temperature, a rise of about 7° ensues, the mixture becomes permeated with minute bubbles of sulphur dioxide, assumes a more viscid character, and on standing for a few minutes the desired compound crystallises out in tiny, colourless needles or leaflets.

The compound obtained in this way fumes strongly in the air, giving off the characteristic odour of sulphur monochloride; it is decomposed by water with a hissing sound, free sulphur being simultaneously precipitated. It is moderately soluble in warm

thionyl chloride and sulphuryl chloride, from the former of which it crystallises out unchanged; its solution in sulphuryl chloride is less stable, as its presence induces the catalytic decomposition of this solvent, both sulphur dioxide and chlorine being evolved on heating.

In order to analyse this compound, a small quantity of the suspension of crystals prepared as above described was drawn into a weighed Gooch crucible through a tube fused into the side of the containing vessel, the bulk of the solvent drawn off by suction, and the last traces were washed out with carbon tetrachloride, the latter being finally removed by a current of dry air. The crucible, containing the pure dry crystalline compound, was then rapidly placed in a large weighing bottle and accurately weighed; the whole was then transferred to a wide-mouthed stoppered bottle partly filled with distilled water, and the weighing bottle so tilted as to cause the lid to roll off and the contents of the crucible to come into contact with the water. After the fumes produced had become completely absorbed, excess of pure nitric acid was added, and the solution filtered from asbestos (originally present in the Gooch crucible) and precipitated sulphur formed by the action of water on the compound. The solution was then made up to a known volume, and the chlorine estimated in the usual manner (Found: in three separate preparations, Cl = 69·2, 69·6, 70·1. Al_2Cl_6,S_2Cl_2 requires Cl = 70·6 per cent.).

Examination of the Chlorinating Properties of the New Reagent. Preparation of Polychlorobenzenes.

In order to avoid repetition, the method adopted in investigating the chlorinating properties of this reagent is here briefly set forth in general terms.

Preparation of the Chlorinating Agent.—In the first place, 25 kilos. of the required chlorinating reagent were made up by running the necessary quantity (250 grams) of sulphur monochloride into a large jar containing sulphuryl chloride; 68·2 grams of this mixture, which for the sake of brevity is subsequently referred to as the chlorinating agent, contains one gram-equivalent of active chlorine or half a gram-molecule of sulphuryl chloride.

General Procedure.—The compound to be chlorinated (generally 1 or 2 mols.) together with finely ground anhydrous aluminium chloride (5—10 grams) was placed in a flask submerged in a water-bath and provided with an efficient reflux condenser, the upper end of which was connected with a second condenser, the latter being loosely packed with asbestos; the two condensers were so arranged that the gases passed up the former and down the latter,

the condensate from the second being returned through a trap to the reaction flask, whilst the gases evolved were conducted through a valve to a vessel containing 10 litres of water in order to absorb the sulphur dioxide and hydrochloric acid evolved during the reaction. By means of this arrangement, all risk is avoided of stopping up the reflux condenser with the solid, highly chlorinated compounds which are volatilised with the gases evolved, and any degree of chlorination can readily be effected. The chlorinating agent (5—10 per cent. excess) was then run down the reflux condenser by means of a suitable dropping funnel, the mixture being cooled or warmed according to the vigour of the reaction, which was completed by warming the bath for a short time, after which the product was washed with water and worked up in a manner dependent on its physical properties.

Where the number of chlorinations to be effected is not great, it will probably be found more convenient to use a single six-bulb reflux condenser and to drop the reagent down this, passing the gases evolved directly from the top of this condenser to the absorption vessel; in this case, the reagent carried off by the gases amounts to abont 15 per cent., so that the quantity added should be adjusted accordingly.

o- *and* p-*Dichlorobenzenes.*—On adding the chlorinating agent (286 grams) to the mixture of chlorobenzene (225 grams) and aluminium chloride (5 grams), the product turns dark-vandyke brown and a vigorous reaction proceeds at the ordinary temperature; this was completed by raising the water-bath to boiling for a few minutes. After being washed with boiling water, 275 grams of an oil were obtained which yielded 190 grams of *p*-dichlorobenzene (m. p. 53°) and 60 grams of an oil which remained liquid at − 10°; this, on freeing from the remaining traces of *p*-dichlorobenzene by conversion into the sulphonic acid and hydrolysing the latter (compare Beilstein and Kurbaton, *Annalen*, 1876, **182**, 94; Friedel and Crafts, *Ann. Chim.*, 1887, [vi], **10**, 413), yielded 37 grams of pure *o*-dichlorobenzene boiling at 178°/758 mm. and having a setting point of − 18° (Found: Cl = 48·13 per cent.).

1 : 2 : 4-*Trichlorobenzene.*—*p*-Dichlorobenzene shows a great tendency to pass straight to the tetrachloro-compound. The best yield of trichlorobenzene is obtained by running the whole of the chlorinating agent (146 grams) at once into the mixture of dichlorobenzene (147 grams) and aluminium chloride (5 grams) contained in a suitable flask and surrounded with cold water. In these circumstances, the mixture gradually turns a deep vandyke-brown and a mild reaction sets in, until the whole of the dichlorobenzene has passed into solution; the water-bath is then filled with ice in order

to control the reaction, which is so vigorous that it is not advisable to operate with larger quantities at a time. After boiling with water, 190 grams of an oil are obtained; this, on fractionation, yields 105 grams of 1 : 2 : 4-trichlorobenzene boiling at 212—213° and setting at 16° (Found: Cl = 58·32 per cent.). From the other fractions, 5 grams of *p*-dichlorobenzene (m. p. 53°) were recovered and 16 grams of 1 : 2 : 4 : 5-tetrachlorobenzene (m. p. 141°).

1 : 2 : 4 : 5-*Tetrachlorobenzene*.—*p*-Dichlorobenzene (294 grams) and aluminium chloride (10 grams) were mixed, the surrounding water-bath was raised to 40°, and the chlorinating agent (582 grams) rapidly run in. The mass, which at first liquefies, rapidly sets to a solid block of almost pure tetrachlorobenzene, or rather the deep moss-green double compound of this substance with aluminium sulphur chloride. The reaction is completed by heating the water-bath to 80° for one hour. On heating the reaction mass with 200 c.c. of water and 200 c.c. of benzene, separating the benzene solution, and allowing it to cool, an almost solid mass of tetrachlorobenzene is obtained; this, on recrystallisation from benzene, yields 249 grams of the pure 1 : 2 : 4 : 5-compound (m. p. 141°) (Found: Cl = 65·74 per cent.). On distilling off the bulk of the solvent, adding an equal volume of absolute alcohol, and allowing to stand over-night, a crystalline deposit was obtained which on recrystallisation yielded a further 53 grams of 1 : 2 : 4 : 5-tetrachlorobenzene; this brings the yield up to 67 per cent. of theory.

Isolation of 1 : 2 : 3 : 5-*Tetrachlorobenzene*.—On fractionating the mother-liquor from three such batches as above (that is, from 882 grams of dichlorobenzene and 1746 grams of the chlorinating agent), 147 grams of a soft, crystalline mass boiling between 233° and 258°/759 mm. were obtained. This was ground up with 300 c.c. of cold absolute alcohol. The residue, 37 grams, consisted chiefly of 1 : 2 : 4 : 5-tetrachlorobenzene and melted, after several recrystallisations, at 140—141°. The alcoholic extract was then concentrated until an oil began to separate, just sufficient alcohol was added to redissolve this at 40°, and the solution was allowed to stand for several days. In this manner, 68 grams of a white, crystalline solid were obtained, which, after several recrystallisations from absolute alcohol, melted at 51° and proved to be the 1 : 2 : 3 : 5-isomeride (Found: Cl = 65·43 per cent.). The yield of the pure substance was 42 grams.

Pentachlorobenzene.—This compound cannot be obtained directly from dichlorobenzene, which, on treatment with the calculated quantity of the new reagent, yields a mixture of tetra- and hexachlorobenzene. Even tetrachlorobenzene shows a great tendency to pass directly to the hexachloro-derivative. A small yield of

the pentachloro-compound can, however, be obtained by proceeding as follows, but the method cannot be recommended for the preparation of pentachlorobenzene.

1 : 2 : 4 : 5-Tetrachlorobenzene (108 grams, finely ground) should first be dissolved in thionyl chloride (1 litre) by the aid of gentle heat, and the solution kept just warm enough to prevent the tetrachloro-compound from crystallising out. To this solution the required chlorinating agent (73 grams) is then added, and, lastly, the anhydrous aluminium chloride (5 grams), which latter should be finely ground and added by degrees under vigorous agitation. The mixture should then be agitated for about eight hours at a temperature of about 40°, after which the reaction is completed by heating at 70—80° for three or four hours. In place of thionyl chloride, carbon tetrachloride may be used as a solvent.

On distilling off about 600 c.c. of the solvent and allowing the residue to cool, a considerable quantity of hexachlorobenzene crystallises out (m. p. 226° after recrystallisation from benzene). The filtrate is then freed from the remaining thionyl chloride by pouring into a large bulk (about 10 litres) of cold water, and the precipitated organic matter ground up with cold absolute alcohol; the residue, which constitutes the bulk of the product, consists chiefly of unchanged tetrachlorobenzene; it melted at 140—141° after recrystallisation. The alcoholic solution is then submitted to fractional precipitation by the addition of water, and the more soluble portions are recrystallised from alcohol; in this manner, a small quantity of a compound melting at 85—86° is ultimately obtained, which analysis proves to be pentachlorobenzene (Found: Cl = 70·22 per cent.).

Hexachlorobenzene.—A mixture of the chlorinating agent (314 grams), finely ground tetrachlorobenzene (216 grams), and aluminium chloride (10 grams) (in place of tetrachlorobenzene, the crude product obtained by treating 147 grams of dichlorobenzene with 291 grams of the chlorinating agent in the presence of 5 grams of aluminium chloride may be used) is warmed to gentle ebullition until the evolution of gas ceases; this occupies about eight hours. On boiling the product out with 800 c.c. of benzene and 100 c.c. of water, separating the benzene solution, and allowing it to cool, the hexachloro-compound crystallises out in beautiful, colourless needles which on recrystallisation melt at 226° (Found: Cl = 74·66 per cent.). The yield amounts to 200 grams of the pure substance, or 70 per cent. of the theoretical.

The author desires to express his thanks to Messrs. A. Boake, Roberts and Co. for supplying the sulphuryl chloride required for

this investigation, and also to Messrs. The United Alkali Co. for the thionyl chloride and dichlorobenzene used.

THE SILBERRAD RESEARCH LABORATORIES,
BUCKHURST HILL, ESSEX. [*Received, April 20th*, 1922.]

CXXI.—*The Aldehydosalicylic Acids and their Derivatives.*

By EDWARD JOHNSON WAYNE and JULIUS BEREND COHEN.

BY the action of chloroform and sodium hydroxide on salicylic acid two isomeric aldehydo-acids are formed which Tiemann and Reimer (*Ber.*, 1876, **9**, 1268), who first studied this reaction, named respectively ortho- and para-aldehydosalicylic acid. These substances, containing as they do three different reactive groups, are specially interesting, but have so far received little attention. We have therefore undertaken a careful examination of them as well as of similar derivatives of other hydroxy-acids, which will form the subject of a future communication. For convenience of nomenclature, the above two acids will be referred to as the 3- and 5-aldehydosalicylic acids.

Preparation of 3- *and* 5-*Aldehydosalicylic Acids.*

The method used, with slight modifications, is that described by Tiemann and Reimer (*loc. cit.*). After precipitating the mixed acids with hydrochloric acid, filtering, and washing, instead of extracting with ether and separating the acids by shaking the ethereal solution with sodium hydrogen sulphite, a simpler and more effective method of separation is to crystallise the mixed acids, after precipitation, from alcohol. The 5-acid, which is the chief product, is much less soluble than the 3-compound or salicylic acid and in this way complete separation of the acid may be effected, with little loss, by not more than two crystallisations. On the average, one-third of the weight of the origiual salicylic acid in the form of the pure 5-compound was obtained. The mother-liquors contain a small quantity of the 3-compound mixed with salicylic acid and some resinous matter, from which the first can be separated by treatment of the ether solution with sodium hydrogen sulphite as described by Tiemann and Reimer.

The Methyl Esters of 3- *and* 5-*Aldehydosalicylic Acids.*

The *methyl* esters were prepared by the action of methyl iodide on the dry silver salts suspended in ether, separating the ether solution, and removing the ether.

The 5-compound crystallises from alcohol in pale buff-coloured needles, m. p. 78°, but may be obtained quite colourless by conversion into the bisulphite compound, reprecipitation, and recrystallisation. It then melts at 82—83° (Found: C = 59·7; H = 4·5. $C_9H_8O_4$ requires C = 60·0; H = 4·44 per cent.). The *ethyl* ester, which was prepared in a similar way, melts at 75°.

The 3-compound, prepared as above, crystallises from alcohol in needles and melts at 87° (Found: C = 60·03; H = 4·77. $C_9H_8O_4$ requires C = 60·0; H = 4·44 per cent.).

Methyl 2-Methoxy-5-aldehydobenzoate.—Three grams of the ester were mixed with 7 to 8 grams of methyl sulphate, and 2 grams of sodium hydroxide in 45 c.c. of water were gradually added while the mixture was gently warmed and shaken. The solid sodium compound first separated and was subsequently replaced by an oily liquid. The solution finally became acid and the excess of methyl sulphate was then decomposed by heating for a short time on the water-bath. On cooling and stirring, the oil solidified. It was ground up with a solution of sodium carbonate to remove the unchanged hydroxy-ester and then crystallised from boiling water, from which it separated in colourless, silky needles, m. p. 86—87°. It is insoluble in sodium carbonate solution, and is readily distinguished from the original hydroxy-ester by the fact that both dissolve in a hot solution of sodium carbonate, but the hydroxy-ester does not separate on cooling, whereas the methoxy-compound crystallises out (Found: C = 61·74; H = 5·22. $C_{10}H_{10}O_4$ requires C = 61·86; H = 5·16 per cent.). Various condensation products were prepared by methods similar to those described on p. 1026. The *phenylhydrazone* crystallises from alcohol in pale yellow needles, m. p. 133—135°; the *nitrophenylhydrazone*, which was obtained by adding a solution of nitrophenylhydrazine to the methoxy-ester, both dissolved in ethyl acetate, was crystallised from pyridine and alcohol and formed clusters of dark red needles, m. p. 200°. The *oxime* crystallises from dilute alcohol in clusters of colourless needles, m. p. 145—147°, and the *semicarbazone* from pyridine in small rectangular plates, m. p. 190°. *2-Methoxy-5-aldehydobenzoic acid* was obtained by hydrolysis of the above ester. It crystallises from water in long, nearly colourless needles, m. p. 170°.

Acyl Derivatives of 5-Aldehydosalicylic Ester.

The *benzoyl* derivative was prepared by dissolving 1 gram of the ester in sodium hydroxide solution; on adding the equivalent quantity of benzoyl chloride and gently warming the mixture with the occasional addition of sodium hydroxide solution, the oily liquid eventually solidified. It was separated, washed, and

recrystallised from a small quantity of alcohol, in which it is very soluble. It crystallises in colourless prisms with pointed ends and melts at 99—101° (Found: C = 67·69; H = 4·39. $C_{16}H_{12}O_5$ requires C = 67·61; H = 4·23 per cent.).

The *acetyl* derivative was obtained by heating 1 gram of the ester with 1 gram of acetyl chloride on the water-bath for half an hour. The product was then poured into water and a little ammonia added to decompose the excess of acetyl chloride. The solid product was crystallised from alcohol and formed colourless needles melting at 81—82° (Found: C = 59·55; H = 4·48. $C_{11}H_{10}O_5$ requires C = 59·45; H = 4·5 per cent.).

Bromination of 5-Aldehydosalicylic Ester.

The ester was dissolved in four times its weight of glacial acetic acid, and an equal weight of bromine in twice its weight of acetic acid was added; the mixture was kept for a short time and then poured into water. The product was filtered, washed, and crystallised twice from dilute alcohol, from which it separated in colourless needles, m. p. 115—116° (Found: C = 41·56; H = 2·84. $C_9H_7O_4Br$ requires C = 41·7; H = 2·7 per cent.). The substance is therefore a monobromo-derivative. The bromine atom probably occupies the 3-position, which is ortho to the hydroxyl and meta to the carboxyl group. The *phenylhydrazone* of the bromine derivative was obtained by dissolving the latter in acetic acid and adding half the weight of phenylhydrazine in the same solvent. The phenylhydrazone was thrown down as a yellow precipitate, which was filtered, washed, and crystallised twice from acetic acid. It forms greenish-yellow needles, m. p. 155—157° (Found: N = 8·17. $C_{15}H_{12}O_3N_2Br$ requires N = 8·05 per cent.).

Nitration of 5-Aldehydosalicylic Ester.

Mononitro-derivative.—Five grams of the ester were slowly added to four times the weight of a mixture of equal parts of fuming nitric acid and concentrated sulphuric acid and cooled to 5°, whilst the temperature was maintained below 10° during the process. When the ester had completely dissolved, the mixture was kept for half an hour, then poured on to ice, and the solid was filtered and washed. It yielded 6·3 grams of the crude nitro-product, which may be crystallised from ethyl acetate or benzene and forms glistening plates, m. p. 161—163° (Found: N = 6·43. $C_9H_7O_6N$ requires N = 6·24 per cent.).

On the addition of sodium hydroxide, the sodium compound separates in the form of clusters of orange needles. The nitro-compound also dissolves in pyridine with a deep yellow colour, indicating the formation of a pyridine salt.

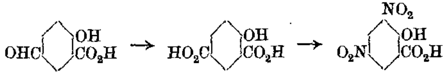
An attempt was made to prepare the *amino*-derivative of the bove by reduction with tin and hydrochloric acid, but no pure roduct could be isolated. After removal of the tin with hydrogen ulphide and evaporating the filtrate, a sticky residue was obtained, rom which no crystalline product could be prepared.

Dinitro-derivative.—In one nitration experiment in which the substance was probably longer in contact with the acid, a second nitro-derivative was isolated similar in appearance to the above nitro-compound but melting at 128—130°. The analysis indicated a dinitro-derivative (Found : N = 10·39. $C_9H_6O_8N_2$ requires N = 10·41 per cent.).

Nitration of 5-Aldehydosalicylic Acid.

Five grams of the aldehydo-acid were added to 25 c.c. of fuming nitric acid, cooled and maintained at about 0—5° in ice. The mixture was left for a few minutes until all was dissolved and then poured on to ice. The yield of the crude nitro-compound was 6 grams. It was purified by converting it into the sodium salt by adding sodium carbonate to the concentrated solution of the nitro-compound. The sodium salt separates in red needles. It was filtered and decomposed with hydrochloric acid. When crystallised from hot water, the nitro-derivative melts at 172—173°, but at 182—183° when crystallised from alcohol. The difference is due to the presence of water of crystallisation in the former compound. The substance proved to be identical with dinitrosalicylic acid prepared from salicylic acid by Hübner (*Annalen*, 1879, **195**, 47), who gives the melting point as 173°. When dehydrated at 120°, it melts at 182°, a fact not mentioned by Hübner. The hydrated acid was analysed (Found : N = 11·58 ; H_2O = 7·74. $C_7H_4O_7N_2,H_2O$ requires N = 11·39 ; H_2O = 7·44 per cent.).

The action of nitric acid is probably to oxidise the aldehyde group to carboxyl, then to replace the carboxyl by splitting off carbon dioxide, and at the same time a nitro-group enters the nucleus in the ortho-position to the hydroxyl group, thus :



Oxidation of 5-Aldehydosalicylic Acid.

The action of permanganate on the acid was examined by Tiemann and Reimer (*Ber.*, 1877, **10**, 1571), who obtained in this way *o*-hydroxy*iso*phthalic acid. We have repeated the process in a slightly modified form as follows : 3·4 grams of the acid were dissolved

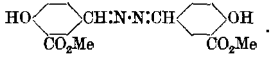
in sodium hydroxide solution containing 1 gram of NaOH in 50 c.c. of water. To this solution 1·5 grams of permanganate in 300 c.c. of water were added. The colour of the permanganate changed at once to brown, and on standing the peroxide separated. On passing in sulphur dioxide, the hydroxy*iso*phthalic acid separated, whilst any unchanged acid remained in solution. The precipitate was filtered, washed, and crystallised from dilute alcohol. The filtrate was concentrated to a small bulk and the unchanged acid precipitated with hydrochloric acid, filtered, and treated with the same quantity of permanganate as before, and if necessary the process was again repeated. In this way, practically the whole of the aldehydosalicylic acid may be oxidised. On heating in a capillary tube, it began to decompose at 285°, turning brown and giving off bubbles of gas. Tiemann and Reimer give 300° as the melting point, but do not refer to any decomposition.

Condensation Products of 5-Aldehydosalicylic Ester.

The *oxime* was prepared by mixing together 0·5 gram of the ester, dissolved in a little alcohol, 0·2 gram of hydroxylamine hydrochloride in water, and 0·15 gram of anhydrous sodium carbonate, also dissolved in water. On warming, a rapid effervescence occurred and a white precipitate was immediately thrown down. It was filtered, washed, and crystallised from dilute alcohol and formed clusters of colourless needles, m. p. 147—148° (Found : N = 7·15. $C_9H_9O_4N$ requires N = 7·18 per cent.).

The *hydrazone* was obtained by mixing together 0·5 gram of ester, 0·43 gram of hydrazine sulphate dissolved in water, and 0·35 gram of anhydrous sodium carbonate dissolved in water. An immediate precipitate was formed and was filtered, washed, and crystallised either from glacial acetic acid or nitrobenzene. From the former it separates in colourless needles, m. p. 239—240°. It is insoluble in alcohol and benzene (Found : N = 7·96. $C_{18}H_{16}O_6N_2$ requires N = 7·91 per cent.).

The compound is therefore a di-aldehydosalicylic ester hydrazone,



The *semicarbazone* was obtained by dissolving 1 gram of the ester in 0·22 gram of sodium hydroxide in 20 c.c. of water and then adding 0·8 gram of semicarbazide hydrochloride. The solution, which was faintly acid, was heated on the water-bath for half an hour, cooled, and the semicarbazone which separated was filtered and washed. It was crystallised from pyridine, from which it separates

small prisms with pointed ends, m. p. 215—216° (Found: = 17·76, 17·68. $C_{10}H_{11}O_4N_3$ requires N = 17·72 per cent.).

In the first experiment, the product was crystallised from glacial acetic acid. It was then found that, on heating, acetic acid was evolved, and analysis showed that the semicarbazone acetate was present (Found: N = 14·32, 14·07, 14·16. $C_{12}H_{15}O_6N_3$ requires N = 14·14 per cent.).

The *phenylhydrazone* was prepared by mixing together concentrated alcoholic solutions containing 0·6 gram of ester and 0·4 gram of phenylhydrazine and heating on the water-bath first with reflux and then in an open vessel until the alcohol was driven off. On cooling and adding a crystal of the phenylhydrazone, the mass solidified and was washed free from phenylhydrazine with light petroleum. It crystallised from alcohol in pale yellow aggregates of blunt prisms, m. p. 120—121° (Found: N = 10·29. $C_{15}H_{14}O_3N_2$ requires N = 10·36 per cent.).

The *nitrophenylhydrazone* was obtained by mixing equal weights of nitrophenylhydrazine and the ester in alcoholic solution. In a short time dark red crystals of the hydrazone separated and were filtered and washed. The substance is slightly soluble in glacial acetic acid or alcohol and insoluble in benzene. It crystallises most readily from nitrobenzene or pyridine (in both of which it is fairly soluble), forming flat prisms with pointed ends. It melts at 265—267° (Found: N = 13·36. $C_{15}H_{13}O_5N_3$ requires N = 13·32 per cent.).

Condensation of 5-Aldehydosalicylic Ester with 1 : 3-*Diketones.*

An attempt was made to condense the aldehydo-ester with aldehydes and ketones and also to apply Knoevenagel's reaction by mixing it with acetoacetic ester, malonic ester, acetylacetone, etc., in presence of alkali or piperidine; but although it was clear that in most cases some condensation had occurred, it was only in the case of acetylacetone that a definite product was isolated. One gram of the ester was dissolved in acetylacetone and a drop of piperidine added. On standing, the mixture solidified, forming brown crystals, m. p. 93—94°. On crystallisation from alcohol, colourless needles were obtained, m. p. 94—95° (Found: C = 64·08; H = 5·41. $C_{14}H_{14}O_5$ requires C = 64·14; H = 5·34 per cent.).

5-Aldehydosalicylic Ester Cyanohydrin.

On adding 10 c.c. of strong sodium hydrogen sulphite solution to 2·5 grams of the ester, in a few minutes the mixture became semi-solid from the formation of the crystalline aldehydo-bisulphite compound. It was separated by filtration and pressed down.

To the moist bisulphite compound 2 grams of potassium cyanide in 5 c.c. of water were added and the mixture was warmed on the water-bath, when a brown oil of the cyanohydrin separated. This was extracted with ether, the ether removed, and the residue heated with concentrated hydrochloric acid to convert the cyanohydrin into the corresponding hydroxy-acid; but although the reaction was repeated with modifications, the original aldehydo-ester was each time regenerated.

2-Hydroxy-3-carboxy- and 4-Hydroxy-5-carboxy-cinnamic Acids.

By the action of acetic anhydride and fused sodium acetate on the 5-aldehydo-acid at the boiling point of the anhydride, slight effervescence occurred, due probably to the splitting off of carbon dioxide. On boiling the resulting mass with potassium hydroxide and acidifying, a viscous, yellow oil was obtained, which could not be crystallised or otherwise purified. Recourse was then had to the method used by Sir W. H. Perkin for the preparation of coumarin (*Annalen*, 1868, **147**, 230), which consists in acting on the sodium salt of the phenol-aldehyde with acetic anhydride and sodium acetate. The sodium salts of the esters were therefore first prepared by dissolving the esters in methyl alcohol and adding the calculated quantity of sodium as sodium methoxide, also in methyl alcohol. A crystalline precipitate was immediately thrown down, which was filtered, washed with alcohol and ether, and dried in a vacuum.

Sodium 5-aldehydosalicylic ester has a straw colour, is slightly soluble in alcohol and insoluble in ether (Found: Na = 11·17. $C_9H_7O_4Na$ requires Na = 11·38 per cent.).

Sodium 3-aldehydosalicylic ester has an orange colour, but in other respects is similar to the 5-aldehydo-ester compound (Found: Na = 11·8. $C_9H_7O_4Na$ requires Na = 11·38 per cent.).

Each of the above compounds was heated with an equal weight of fused sodium acetate and 2·5 parts of acetic anhydride at 160° for four to five hours. The resulting dark-coloured mass was boiled with potassium hydroxide solution, filtered from a small quantity of resinous matter, and the cinnamic acid precipitated by the addition of hydrochloric acid. After recrystallisation from water or dilute alcohol, the two acids were obtained as straw-coloured, crystalline powders very similar in appearance. *4-Hydroxy-5-carboxycinnamic acid* was analysed (Found: C = 57·41; H = 4·03. $C_{10}H_8O_5$ requires C = 57·69; H = 3·84 per cent.).

On heating, *2-hydroxy-3-carboxycinnamic acid* melts, darkens, and evolves water and carbon dioxide, and at the same time a crystalline substance sublimes in colourless needles, which can be

stallised from hot water. It possesses the m. p. and the char-
ristic smell of coumarin.

$$CO_2H\cdot C_6H_3<^{CH:CH\cdot CO_2H}_{OH} = C_6H_4<^{CH:CH}_{O-CO} + H_2O + CO_2.$$

is experiment therefore determines the position of the aldehyde
oup in the 3-aldehydo-acid.

Owing to the difficulty of obtaining the 3-aldehydo-acid in suffi-
nt quantity, we have been unable to prepare a complete set of
rivatives of this substance; but we hope to improve the yield
d to publish further results in a subsequent paper.

We desire to acknowledge our indebtedness to the Research Fund
ommittee of the Chemical Society for a grant towards the cost
materials for this research.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS. [Received, May 4th, 1922.]

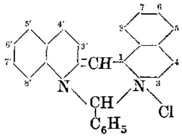
CXXII.—isoQuinoline and the isoQuinoline-Reds.

By JOHN EDMUND GUY HARRIS and WILLIAM JACKSON POPE.

ALTHOUGH large quantities of *iso*quinoline are represented by the small percentage of this important base present in coal-tar, no ready method for its extraction in a state of purity has been previously described. Hoogewerf and van Dorp (*Rec. trav. chim.*, 1885, **4**, 125; 1886, **5**, 306) first separated *iso*quinoline by fractional crystallisation of the acid sulphate formed from coal-tar quinoline; according to Weger (*Z. angew. Chem.*, 1909, **22**, 394), coal-tar quinoline is accompanied by only about 1 per cent. of *iso*quinoline, so that its separation by the Dutch workers involved very skilful and tedious operations. Weissgerber (*Ber.*, 1914, **47**, 3175; D.R.-P. 285666) showed the way to a more rapid method of separation by pointing out that *iso*quinoline is a much more powerful base than quinoline; he treats coal-tar quinoline in benzene solution with sufficient sulphuric acid to combine with about one-sixth of the base and obtains in this way an extract which is proportionately richer in *iso*quinoline than is the original mixture of the bases; *iso*quinoline is then separated from the mixture of bases which passes into the sulphuric acid by fractional crystallisation of the acid sulphate from alcohol. On repeating Weissgerber's method, as he describes it, we were able to separate only about 3 grams of impure *iso*quinoline hydrogen sulphate from 1,200 grams of coal-

tar quinoline. By utilising the principle suggested by Weissgerber, and multiplying its application a number of times in a simple manner, we have been able to devise an easy means for separating pure *iso*quinoline in quantity from coal-tar quinoline.

Considerable interest attaches to the dyestuff *iso*quinoline-red which was first obtained by Jacobsen (D.R.-P. 19306 and 40420) by heating coal-tar quinoline with benzotrichloride; Vogel showed it to be a powerful photographic sensitiser (D.R.-P. 39779) and it is still largely used as such. Hofmann found that the dyestuff is produced by the interaction of *iso*quinoline, quinaldine, and benzotrichloride and that the condensation is promoted by the presence of zinc chloride (*Ber.*, 1887, **20**, 9); the constitution of *iso*quinoline-red has been determined by Vongerichten and his co-workers (*Ber.*, 1910, **43**, 128; 1912, **45**, 3446) to be represented by the formula



Using zinc chloride as the condensing agent, we found, as Hofmann did, that the *iso*quinoline-red is only freed from inorganic matter with difficulty; each 100 parts of *iso*quinoline yielded less than 50 parts of the dyestuff. By using aluminium chloride as the condensing agent, we have obtained a yield of about 70 parts of pure dyestuff from each 100 parts of *iso*quinoline and are able to free the latter much more easily from inorganic impurities. In the present paper we describe the preparation of several colouring matters of the *iso*quinoline-red class.

Preparation of iso*Quinoline.*

The commercial coal-tar quinoline fraction was distilled through a good dephlegmating column and separated into portions boiling at 220—230°, 230—235°, 235—245°, and 245—255°; the fraction boiling at 220—230° did not give a satisfactory yield of *iso*quinoline, and the higher fractions boiling at 230—255° are best used for the separation by the method now described.

The rectified base (387 grams) is shaken vigorously with 4*N*-sulphuric acid (600 c.c.) in a separating funnel for half a minute; the undissolved base (about 20 per cent. of the whole) is removed with the aid of a little benzene. The sulphuric acid solution is then similarly extracted with a 4*N*-ammonia solution

0 c.c.) in sufficient quantity to remove 20 per cent. of its con-
its in base; the liberated bases are removed by extraction with little benzene as before. The treatment with ammonia and e extraction with benzene are repeated, sufficient ammonia ing added on each occasion to liberate 20 per cent. of the basic nstituents from the sulphuric acid solution. After eleven repeti-ons of the ammonia treatment, only 6·9 per cent. (26·7 grams) of e original base remains in the sulphuric acid solution; the whole the base is then liberated by addition of ammonia and extracted ith a little benzene. Successive quantities of the original quinol-e fraction are treated in the manner described until a sufficient nount for further purification is obtained; by the treatment of ,500 grams of the original fraction and distillation of the final enzene extract, 100 to 110 grams of base containing 20 to 30 per ent. of *iso*quinoline can be obtained.

The distilled base is now dissolved in twice its volume of rectified pirit, and the calculated amount of concentrated sulphuric acid equired to form the acid sulphate slowly added from a dropping unnel, the solution being mechanically stirred and the temperature eing kept below 30°. Crystallisation sets in immediately and the cid sulphate is filtered off and crystallised two or three times from ight to nine parts of boiling alcohol until its melting point rises to 206·5°. This product is pure *iso*quinoline hydrogen sulphate and on treating it with ammonia, extracting with benzene, and distilling the benzene extract, the boiling point rises sharply to 242·5° and pure *iso*quinoline passes over.

By this method of preparation, which is very rapidly carried out, the coal-tar quinoline fraction yields 1·5 per cent. of its weight of pure *iso*quinoline.

*iso*Quinoline is a colourless oil with an odour recalling those of benzaldehyde and of aniseed and quite dissimilar to the odour of quinoline; the difference in odour between quinoline and *iso*quinol-ine is comparable with that between α- and β-naphthylamines. On cooling under tap-water it solidifies to a white crystalline mass which melts at 24·25°; it boils at 242·5° (thread in vapour) under 760 mm. pressure. This boiling point is higher than those previously recorded; Hoogewerf and van Dorp (*loc. cit.*) give 240·5°/763 mm. and Pictet and Gams (*Ber.*, 1910, **43**, 2391) give 240°/730 mm. It seemed therefore of interest to determine the boiling points of pure quinoline and quinaldine, and several samples were examined; we find that quinoline boils at 236·5°/760 mm. and quinaldine at 247·2°/760 mm. The difference of six degrees between the boiling points of quinoline and *iso*quinoline is greater than has been hitherto stated.

*iso*Quinoline-Red.

*iso*Quinoline (5 grams), quinaldine (5·2 grams), and anhydrous aluminium chloride (2·5 grams) are mixed in a boiling-tube, when heat is evolved; the mixture is maintained at 90° in an oil-bath and benzotrichloride (7·6 grams) added. The temperature is then raised to 150—155° for an hour, after which the solid melt is taken up in a little dilute alcohol and the product mixed with milk of lime [1 litre of 10 per cent. $Ca(HO)_2$]. The solution is now distilled in a current of steam for three hours, the unchanged basos beiug recovered, and thc boiling solution (1·5 litres) filtered, the filtrate being treated with hydrochloric acid (15 c.c.). On cooling, the dyestuff (4·2 grams) crystallises and is found to be free from inorganic matter; it is conveniently recrystallised from boiling water (380 c.c. for each gram of crystals), hydrochloric acid (1 c.c. to each 100 c.c. of solution) being added before crystallisation occurs (Found: C = 79·1; H = 5·1; N = 7·29. $C_{26}H_{19}N_2Cl$ requires C = 79·0; H = 4·8; N = 7·10 per cent.).

The initial yield of dyestuff obtained by the method just described is about 50 per cent. greater than that given by the method of Vongerichten and Homann and the final yield is much larger owing to the absence of inorganic impurities in our product.

*6′-Methyl*iso*quinoline-Red.*

A mixture of *iso*quinoline (5 grams), *p*-toluquinaldine (5·7 grams), aluminium chloride (2·5 grams), and benzotrichloride (7·6 grams) is treated in the manner described above; the deposited dyestuff (2·3 grams) is free from inorganic matter and is further purified by recrystallisation from boiling dilute hydrochloric acid. The substance crystallises in minute, red needles and is dried in a vacuum at 150° previous to analysis (Found: C = 79·3; H = 5·3; N = 6·83. $C_{27}H_{21}N_2Cl$ requires C = 79·3; H = 5·2; N = 6·85 per cent.). Very much smaller yields than that stated are obtained when zinc chloride is used as the condensing agent.

*6′-Ethyl*iso*quinoline-Red.*

This substance is prepared by the method described above, 6-ethylquinaldine (6·63 grams) being substituted for the *p*-toluquinaldine; the crude dyestuff is purified with greater difficulty than in the previous instances and four extractions, each with 1 litre of boiling milk of lime, are desirable. The product (2·3 grams) is recrystallised from boiling dilute hydrochloric acid, but retains a small proportion of inorganic matter with great tenacity; this latter is removed by boiling with *N*/10-sodium carbonate for five minutes,

lifying the solution, and allowing it to crystallise. The substance leposited in minute, crimson crystals and is dried first at 100° l then at 150° in a vacuum (Found: C = 79·0; H = 5·5. $H_{23}N_2Cl$ requires C = 79·5; H = 5·4 per cent.).

The methyl and ethyl derivatives now described behave as otographic sensitisers in a manner almost identical with the parent quinoline-red; they are, however, much less soluble in water an the latter.

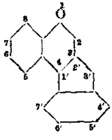
THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, May 10th*, 1922.]

XXIII.—*A Synthesis of* iso*Brazilein and certain Related Anhydropyranol Salts. Part II.* Synthesis of* iso*Hæmatein.*

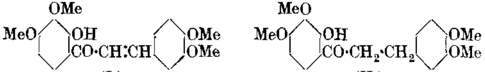
By HERBERT GRACE CRABTREE and ROBERT ROBINSON.

N Part I of this investigation (T., 1918, **113**, 859), a method of ynthesis of *iso*brazilein salts was described, and the present communication is partly of a supplementary character and partly a record of the extension to the synthesis of *iso*hæmatein. Reference may be made to the introductory remarks in the earlier publication for a more detailed explanation of the processes employed and of the relation of the results to the elucidation of the constitutional problems presented by brazilin and hæmatoxylin. The synthesis of *iso*hæmatein has been effected in the following manner. Veratrylidenegallacetophenone dimethyl ether (I) was found to be readily reduced to its dihydro-derivative (II) by means of hydrogen in alcoholic solution at 50—60° and in presence of palladium.

* The nomenclature used in this communication is based on the scheme shown below and leaves no ambiguity in regard to the position of fusion of the benzopyrylium and indene nuclei.

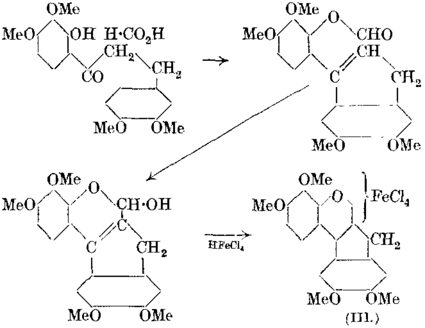


It is not permissible to transpose *iso*hæmatein ferrichloride tetramethyl ether to *iso*hæmatein tetramethyl ether ferrichloride. The reason is given in T., 1918, **113**, 860 (footnote).



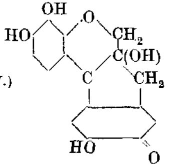
(I.) (II.)

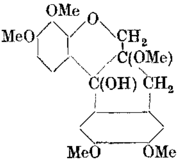
On boiling with absolute formic acid and anhydrous zinc chloride, *this ketone is changed into an isohæmatein tetramethyl ether salt*, which was isolated as the ferrichloride (III). The reaction occurs, in all probability, in accordance with the scheme:



(*Pseudo-base, a-pyranol.*) (III.)

The oxonium salt (III) was found to be identical in all respects with the ferrichloride obtained by Engels, Perkin, and Robinson (T., 1908, **93**, 1152) from hæmatein (IV) through pentamethyldihydrohæmateinol (V), which is one of the chief products of the action of methyl sulphate and potassium hydroxide on the colouring matter.

(IV.)




(V.)

V loses methyl alcohol and water under the influence of sulphuric acid and is converted to an oxonium sulphate, from which the ferrichloride (III) is obtained by the action of hydrochloric acid

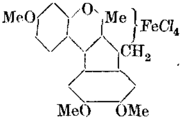
and ferric chloride. This compound is characterised by a definite melting point and by other properties which enable the identification of the synthetical product with that obtained from hæmatoxylin to be made with certainty. It is otherwise with the amorphous *iso*hæmatein, the preparation of which from the ferrichloride is described on p. 1041. Nevertheless, the *iso*hæmatein obtained synthetically in this way had all the properties of the substance prepared from hæmatoxylin by Hummel and A. G. Perkin (T., 1882, **41**, 373).

E X P E R I M E N T A L.

Synthesis of iso*Brazilein.*

The synthesis of *iso*brazilein ferrichloride trimethyl ether (Crabtree and Robinson, *loc. cit.*) has been repeated on a larger scale, and some further details of the procedure adopted in demethylating the substance can now be recorded. The ferrichloride trimethyl ether (2·6 grams) was very gently warmed with a little concentrated sulphuric acid in a vacuum and the orange, sparingly soluble sulphate precipitated by the addition of water. After a second solution and precipitation, the salt was collected, washed with dilute sulphuric acid, and heated with concentrated hydrochloric acid (20 c.c.) during four hours at 150—160°. The contents of the tube were washed out with water, the mixture boiled with a little animal charcoal and filtered, the filter being washed with hot dilute hydrochloric acid. The orange solution was evaporated in a vacuum to very small bulk and the pasty residue dissolved in the minimum amount of hot dilute hydrobromic acid. On cooling, the *iso*brazilein hydrobromide separated in dark reddish-orange prisms, and after recrystallisation the characteristic appearance under the microscope was identical with that of a specimen of the substance, prepared by the action of sulphuric acid followed by hydrobromic acid on brazilein. A careful comparison disclosed no differences existing between the two substances. In sulphuric acid they both gave a yellow solution with bright green fluorescence, whilst in dilute aqueous sodium hydroxide they dissolved to rich bluish-red (damson) solutions which behaved similarly on dilution with water. The addition of sodium acetate to the suspension and solution of the salt in water gave in each case a dark mauve precipitate of *iso*brazilein (anhydrobrazilein). A portion of the synthetical specimen was collected, washed, and dried, and gave a negative result in a Zeisel determination. Finally, dye-trials on cloth mordanted with aluminium gave identical brilliant alizarine-red shades with the synthetical *iso*brazilein and that obtained from brazilin (compare Hummel and Perkin, *loc. cit.*).

7 : 5′ : 6′-Trimethoxy-2-methyl-3 : 4-indeno(2′ : 1′)-benzopyrylium Ferrichloride (*Methylisobrazilein Ferrichloride Trimethyl Ether*),



A mixture of dihydrobutein trimethyl ether * (2 grams), zinc chloride (2 grams), and acetic anhydride (15 c.c.) was boiled during ten minutes. The solution became carmine and then orange-red and a bright green fluorescence developed. Finally, the liquid became brown and, at the end of the reaction, the addition of acetic acid (10 c.c.) and of a saturated solution (15 c.c.) of ferric chloride in concentrated hydrochloric acid precipitated the oxonium ferrichloride as a brown powder. This was collected, washed with hot acetic acid, dissolved in water containing three drops of concentrated hydrochloric acid, and the ferrichloride again precipitated from the filtered solution by the addition of an excess of ferric chloride dissolved in hydrochloric acid. The light brown precipitate was filtered off, washed with dilute hydrochloric acid containing ferric chloride, well drained, and added to boiling acetic acid. Although the ferrichloride is very sparingly soluble in this solvent, it will dissolve when obtained in the above manner from aqueous solution, but the liquid must be filtered at once and, however expeditiously the operation is carried through, there will always be a certain amount of yellow, crystalline residue (*A*). The filtrate deposited intensely brown, shining, microscopic prisms (*B*). These are of rhombic habit and show a strong tendency to twin with formation of paddle-shaped aggregates. The substance also crystallises from hot dilute hydrochloric acid containing ferric chloride in orange needles (*C*) with green, metallic reflex, and, most convenient of all, in brown, microscopic prisms by adding ethyl alcohol to a

* The authors greatly regret that at the time of their previous communication they had overlooked the fact that Bargellini and Finkelstein (*Gazzetta*, 1912, **42**, 10) obtained this substance by the catalytic reduction of the corresponding unsaturated ketone. Bargellini and Lidia (*ibid.*, 1914, **44**, 27) also obtained the monomethyl ether of 2 : 4-dihydroxyphenyl β-phenylethyl ketone by the reduction of benzylidenepæanol and found this substance to melt at 103—104° (Crabtree and Robinson, *loc. cit.*, give 105°), further stating that the melting points given by Bargellini and Marantonio (*ibid.*, 1908, **38**, 514) for the mono- and di-methyl ethers of the phenylpropionylresorcinol should be transposed. The present authors, however, employing the conditions recommended for the production of the dimethyl ether, have only succeeded in obtaining the monomethyl ether melting at 105°.

;entrated solution in acetone (*D*). The four specimens gave tions which had identical properties and were analysed after hing with acetic acid and drying at 120° after preliminary *ing in a vacuum* [Found: (*A*) C = 45·8; H = 3·9, (*B*) C = 46·2; = 3·8; Fe = 10·6; Cl = 26·8, (*C*) Cl = 26·9, (*D*) C = 46·3; = 3·8. $C_{20}H_{19}O_4FeCl_4$ requires C = 46·1; H = 3·6; Fe = 10·7; = 27·2 per cent.].

:he substance darkened from about 210° and melted with omposition at 226—227°. As indicated above, this salt has a dency to crystallise in variously coloured modifications, greenish-low, orange, coffee-brown, and chocolate-brown have been served, but these are probably not chromoisomerides and the ears on paper are in most cases indistinguishable. The differing es of the crystals and minute amounts of coloured impurities pear to be the factors which determine the property of colour. ıe substance dissolves in water to a yellow solution with vivid anium-green fluorescence, and, although extremely sparingly luble in cold acetic acid and alcohol, it is sufficiently so to impart is fluorescence to the solution. On boiling with alcohol, a ·llowish-brown solution with a most intense ivy-green fluorescence obtained. The salt is sparingly soluble in chloroform, and this ›lution exhibits only weak fluorescence. It is insoluble in cold enzene and sparingly soluble in the hot solvent to a yellow, non-uorescent solution. The ferrichloride dissolves readily even in old acetone to a strongly fluorescent solution, which remains clear ut loses its fluorescence on the addition of benzene. A suspension ı acetic acid was treated with concentrated nitric acid. The first ew drops intensified the fluorescence, but this soon diminished gain and finally disappeared. On the addition of water, a yellow recipitate was thrown down and this dissolved in benzene to a lichroic red and green solution from which light petroleum pre-:ipitated brownish-red flocks, leaving a green solution.

7 : 5′ : 6′-Trimethoxy-2-ethyl-3 : 4-indeno(2′ : 1′)-benzopyrylium Ferrichloride.

This substance was obtained by substituting propionic anhydride for acetic anhydride in the process described in the preceding section, but, as the reaction proceeded more slowly, the time of heating was extended to twenty minutes. The ferrichloride precipitated from the reaction mixture was collected and crystallised from acetic acid, being obtained in glistening, orange-yellow clusters of needles, which appear to contain solvent of crystallisation. The melting points observed were variable and depended on the rate of heating. The substance was dried in a vacuum at 110° until

constant in weight, but the loss did not correspond with any definit molecular proportion of water or acetic acid. This is probably du to loss in the process of air-drying at the ordinary temperatur (Found: C = 47·3; H = 4·0. $C_{21}H_{21}O_4FeCl_4$ requires C = 47·1 H = 3·9 per cent.).

This substance differs from its lower homologue just described i being much more soluble in solvents, but it closely resembles it i all other respects. It is readily soluble in chloroform, and all it solutions, except that produced by the addition of benzene to th substance dissolved in acetone, exhibit brilliant yellowish-gree fluorescence. The behaviour with acetic and nitric acids is th same as that of the analogous methyl derivative.

2-Hydroxy-3 : 4-dimethoxyphenyl β-Veratrylethyl Ketone (II).

This substance was obtained in almost theoretical yield by mean of the following process. Veratrylidenegallacetophenone dimethy ether * (Kostanecki and Rudse, *Ber.*, 1905, **38**, 936) (4 grams) wa

* Some improvements in the preparation of this substance may be note Gallacetophenone (Nencki and Sieber, *J. pr. Chem.*, 1881, [ii], **23**, 538) wa obtained by heating under reflux a mixture of pyrogallol (50 grams), glaci acetic acid (75 grams), and fused zinc chloride (75 grams) during six hour at 150° (thermometer in the mixture). Ether was added to the cooled pro duct so as to dissolve all but a little of the zinc chloride, and this solutio was successively washed with a little concentrated hydrochloric acid, 10 pe cent. aqueous hydrochloric acid, and twice with a little water. The extra was then dried over calcium chloride, filtered and evaporated, and the residu taken up with alcohol. Hot water was then added until incipient precip tation and, on cooling, long, colourless needles of gallacetophenone separate the yield of pure substance amounting to 36 grams. The methylation c gallacetophenone under various conditions was investigated and the be results obtained by the following method (compare A. G. Perkin, T., 189 **67**, 997). A mixture of gallacetophenone (10 grams), methyl sulphate (22· grams), anhydrous potassium carbonate (24·7 grams), and freshly distille nitrobenzene (200 c.c.) was maintained at the point of gentle ebullition b heating in an oil-bath during six hours. The nitrobenzene was then remove in a current of steam and the residue acidified with hydrochloric acid an extracted with ether. Unchanged and monomethylated materials we removed by washing the ethereal solution with dilute aqueous sodium carbo ate, after which the dimethyl ether was extracted by washing with successiv small volumes of dilute aqueous sodium hydroxide. On acidification of th separated and combined extracts, the gallacetophenone dimethyl eth separated in a crystalline form and was collected and recrystallised fro alcohol. The yield was 5 grams and could be increased by working up th unchanged and monomethylated products. The condensation of gallacet phenone dimethyl ether and veratraldehyde gave almost theoretical yiel under the following conditions. Fifty per cent. aqueous potassium hydroxi (25 grams) was added to a hot solution of gallacetophenone dimethyl eth (13 grams) and veratraldehyde (11 grams) in ethyl alcohol (130 c.c.). Aft shaking, the mixture was maintained at 60—70° during four hours and the

dissolved in alcohol (200 c.c.) at 60—65° contained in a flask which could be vigorously agitated and filled with hydrogen.

After displacing the air in the apparatus, palladious chloride (10 c.c. of 1 per cent. aqueous solution) was added and the flask, connected with the hydrogen supply, shaken during half an hour. The gas was rapidly absorbed and the solution became nearly colourless. In order to complete the reduction the temperature of the liquid was again raised to 60° and the shaking continued for a further period of thirty minutes, the vessel being connected as before with the hydrogen generator. The solution was then filtered from suspended palladium and concentrated, when the remainder of the palladium, held in colloidal solution, separated. At a suitable stage the liquid was again filtered, and, on cooling, deposited silvery leaflets, melting after recrystallisation from alcohol at 88° (Found: C = 65·8; H = 6·5. $C_{19}H_{22}O_6$ requires C = 65·9; H = 6·3 per cent.).

This substance is readily soluble in most organic solvents. Its alcoholic solution gives an intense brownish-violet coloration on the addition of ferric chloride. It is soluble in very dilute aqueous sodium hydroxide, and the addition of more sodium hydroxide precipitates a sodium derivative. Ether, however, is able to extract the substance almost completely from an alkaline solution.

iso*Hæmatein Ferrichloride Tetramethyl Ether* (III).

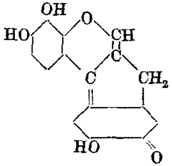
Hydroxydimethoxyphenyl β-veratrylethyl ketone (2 grams) was dissolved in anhydrous formic acid (20 grams) and, after the addition of fused zinc chloride (5 grams), which produced a brilliant carmine coloration, the solution was boiled under reflux during eight hours, in the course of which the red colour faded and changed to brownish-yellow. A ferrichloride was precipitated as a brown powder by the addition of dilute hydrochloric acid and a concentrated solution of ferric chloride in concentrated hydrochloric acid to the cooled reaction product. This was collected, dried, and thrice crystallised from glacial acetic acid. It was obtained in this way in glistening, brown needles which, in spite of their attractive appearance, were not yet quite pure and were recrystallised from chloroform. It was found best to filter a hot saturated solution and rapidly distil away two-thirds of the chloroform. The substance separated, on cooling, in hæmatite-red needles with green reflex. Under the

cooled and acidified with hydrochloric acid. The copious yellow precipitate was collected and crystallised from 90 per cent. alcohol, from which the substance separated in slender, pale yellow needles melting at 125° (Kostanecki and Rudse, *loc. cit.*, give 124°).

microscope, these are seen to be transparent, orange, short, unpointed prismatic needles, which are very well shaped and frequently twin and form clusters (Found: C = 45·0; H = 3·7. $C_{20}H_{19}O_5FeCl_4$ *requires* C = 44·9; H = 3·6 *per cent.*).

This salt darkens slightly above 170° and melts at 191° with decomposition. It melted at the same temperature when mixed with a specimen obtained as described on p. 1034 from hæmatoxylin and crystallised from chloroform (Engels, Perkin, and Robinson, *loc. cit.*, give m. p. 190° for the substance crystallised from acetic acid). In crystal form, appearance in mass, solubilities, and in every other respect, the two specimens were identical. The yellow, aqueous solution becomes nearly colourless on great dilution and the colour can then be restored by the addition of hydrochloric acid. Addition of sodium acetate to an aqueous solution produces a brown, flocculent precipitate, which is partly soluble in ether to a faint pink solution. The separated ethereal layer gives an orange precipitate on shaking with hydrochloric acid, and this substance crystallises from hot dilute hydrochloric acid in orange, microscopic needles. It is the indenobenzopyrylium chloride, and is converted by ferric chloride to the ferrichloride, melting, after crystallisation, at 191°. Evidently the pseudo-base corresponding with these oxonium salts exists in the ethereal solution, but attempts to obtain the substance in a crystalline form were unsuccessful. The ferrichloride is insoluble in cold alcohol and does not even colour the liquid. On boiling, a deep yellow solution is obtained, but nothing separates on cooling, and some decomposition must have occurred. The solution of the ferrichloride in sulphuric acid is intensely yellow and exhibits a green fluorescence, very weak by comparison with that of similar resorcinol (brazilin) derivatives.

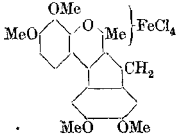
*iso*Hæmatein (*Anhydrohæmatein*),



Synthetical *iso*hæmatein ferrichloride tetramethyl ether was demethylated exactly as described above in the case of the related brazilin derivative (p. 1035), except that the orange sulphate was converted to the hydrochloride by crystallisation from dilute hydrochloric acid before proceeding. The resulting *iso*hæmatein hydrochloride crystallised from dilute hydrochloric acid in deep orange microscopic needles, and comparison showed it to be identical

with the salt prepared from hæmatein as directed by Hummel and Perkin (*loc. cit.*). On the addition of silver hydroxide to its aqueous solution and evaporating the filtered liquid to dryness, the characteristic green lustre of the residual *iso*hæmatein was observed. This substance dissolved in dilute potassium hydroxide to a reddish-violet solution, which became darker in shade, although less intensely coloured, on standing. The brownish-red shades given by the synthetical *iso*hæmatein hydrochloride and that obtained from hæmatoxylin on aluminium-mordanted cloth were identical and behaved in the same way on soaping and on treatment with sodium hypochlorite solution.

7 : 8 : 5′ : 6′-*Tetramethoxy-2-methyl-3 : 4-indeno(2′ : 1′)-benzopyrylium Ferrichloride*,



This substance was prepared from hydroxydimethoxyphenyl β-veratrylethyl ketone, acetic anhydride, and zinc chloride under precisely the same conditions as those employed in the case of the corresponding resorcinol derivative (see p. 1036). The ferrichloride precipitated from the reaction mixture was dried and crystallised from acetic acid or by the addition of alcohol to a concentrated solution in acetone (Found: C = 45·7; H = 3·9. $C_{21}H_{21}O_5FeCl_4$ requires C = 45·7; H = 3·8 per cent.).

This homologue of *iso*hæmatein ferrichloride tetramethyl ether closely resembles it in most of its properties and crystallises in deep brown, dense aggregates of microscopic needles, melting at 192—193° with decomposition. On the addition of sodium acetate to a mixture of its yellow aqueous solution and ether, the water is coloured red and the ether bluish-green, the latter quickly changing to dull mauve. The ethereal layer now contains the pyranol base and gives a flocculent, brown precipitate, insoluble in ether and water, on the addition of picric acid. The pseudo-base was also treated with hydrochloric acid and ferric chloride and the ferrichloride, m. p. 192—193°, regenerated.

UNIVERSITY OF LIVERPOOL (1919).
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UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
THE UNIVERSITY, ST. ANDREWS. [*Received, April 7th*, 1922.]

CXXIV.—*A Property of Ethyl Tartrate.*

By Thomas Stewart Patterson.

In the March number of this Journal (this vol., p. 532) there appears a paper by Messrs. Lowry and Cutter dealing with ethyl tartrate, in which they state (i) that " almost all commercial samples of ethyl tartrate are yellow in colour," a similar colour having been also observed in one of their own samples. " This colour is undoubtedly due to an impurity, since it can be removed by freezing out and centrifuging the crystalline ester." And, (ii), " The purified ester developed a yellow colour when heated in the distilling flask, and gave a yellow distillate, the colour of which disappeared, however, after a few hours." This colour, they regard as an indication of *purity* rather than of *impurity* in the sample (pp. 537–538) and they regarded it as perhaps the result of a reversible dehydration (p. 544).

Since 1895 I have been aware that under certain circumstances ethyl tartrate may develop a transient green colour and from time to time I have carried out experiments on this subject, but since these have not reached the stage I should have wished, they have not previously been referred to. In view, however, of Lowry and Cutter's work I should like now to indicate briefly the conclusions which have so far been arrived at. The green substance which Lowry and Cutter rightly regard as an impurity, and which can be fractionated out of the ester, possesses the remarkable property not mentioned by them that, when present in the ethyl tartrate in quantities not too large, it becomes perfectly colourless on standing for some time. The impurity therefore possesses the characteristic which Lowry and Cutter attribute to specially pure ethyl tartrate.

Since substances the colour of which fades on standing and returns again on re-heating are uncommon and possess a peculiar interest, the matter is perhaps one of importance, and I have therefore constantly kept it in mind. The first indication of the cause of this green colour was given by a slight accident during distillation, whereby a considerably too rapid stream of air was sucked for a short time through the ester at a temperature of about 200°. The first runnings in the distillation then came over bright green, almost grass green, in colour, but on standing for a time became colourless or practically so. Even in such a case, however, the substance producing this effect is probably present only in small quantity, since it does not much lower the rotation of the ester; but that it is not an indication of purity in the ethyl tartrate but merely an

impurity seems to be certain from the fact that it may be almost completely—or completely—fractionated out of the ester. It is quite certain that on distilling a sample of such ethyl tartrate the first runnings are very much more green than the later fractions. Some twenty years ago, at Leeds, Mr. W. Lowson, B.Sc., was good enough to carry out for me a few experiments in this connexion. Ethyl tartrate prepared by the hydrochloric acid saturation method was heated to a temperature of about 200°, and then a stream of air was sucked through the ester. We hoped in this way to obtain a considerable quantity of the green product, but our collaboration had to be discontinued before we had succeeded in our efforts. It may be recorded, however, that in one experiment, after the heating had been carried on for some time, the whole contents of the flask suddenly became converted into a carbonaceous mass. We have not been able to find a method for isolating the impurity, possibly because it is present in only small quantity mixed with a large proportion of ethyl tartrate. If the impurity is present in sufficient quantity it may impart a permanent green colour to the ethyl tartrate. On heating a colourless sample of ester of this kind, the green colour develops at a temperature of about 120°, and it is also noticeable that, conversely, although both the liquid trapped in the neck of a Claisen distilling flask and the hot vapour in the neck of the flask may appear quite colourless, the distillate may, nevertheless, be distinctly green.

Since the appearance of Lowry and Cutter's paper the foregoing observations have been verified. A bottle is kept in this laboratory labelled *green ethyl tartrate* and to it are consigned any samples which have become green during preparation, as it is preferable to use only pure and colourless products. Some of this specimen, which exhibited, permanently, a slight green colour, was very carefully distilled at a pressure between 1 and 2 mm., from a Claisen flask with a high side tube. The tartrate boiled in the neighbourhood of 117° with the oil-bath at a temperature of about 157°. The first fraction was bright green, and three successive fractions showed a rapidly diminishing colour. The last fraction had only the faintest tinge of green. All, except the first, became perfectly colourless on standing for a time. It is thus evident that the green substance can be fractionated out; it is also evident that it is no ordinary impurity.

The distillation was stopped when nearly half of the original ester remained in the flask. This was then heated to a temperature of about 200° on an oil-bath, and air was sucked through the hot ester for a few minutes. Distillation at low pressure was then recommenced, and the first fraction came over almost grass-green in

colour. The coloured impurity, doubtless an oxidation product, had been re-formed.

I propose to continue the investigation of this remarkable phenomenon.

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UNIVERSITY OF GLASGOW. [*Received, April 6th*, 1922.]

CXXV.—*Capsularin, a Glucoside from Jute Leaf.*

By HARIDAS SAHA and KUMUD NATH CHOUDHURY.

THE glucoside present in the seeds of *Corchorus capsularis* has been described, under the name of corchorin, by Tsuno (*Monatsh. Tierheilkunde*, 1895, **6**, 455) and by Kobert (*Ber. Natur. Ges. Rostock ; Arch. Freunde Natur. Ges. Mecklenburg*, 1906, No. 5; *Chem. Zentr.*, 1907, i, 1273). No one, however, seems to have done any work with the leaves of the same plant, which too appear to contain a glucoside. The dried leaves of this plant, commonly known as jute, have long been used in medicine in Bengal under the name of *nalita*. The corchorin of Kobert, which he obtained from Merck, is a brown, amorphous powder, which is much more bitter than quinine sulphate and turns bluish-green with concentrated sulphuric acid. The glucoside obtained from the leaf of the same plant and described below, for which the name *capsularin* is proposed, seems to be different from corchorin, as it is a white, crystalline substance which is much less bitter than quinine sulphate and develops a red coloration with sulphuric acid.

Matured leaves of the plant, collected in June and July and dried in the sun, were extracted with boiling water, and the extract was clarified with lead acetate, freed from lead by hydrogen sulphide, and concentrated to a small bulk after the addition of a little ammonia. The glucoside, precipitated by tannic acid from this dark-coloured liquid, was again liberated with barium hydroxide solution, the barium removed with carbon dioxide, and the filtrate concentrated and kept over-night, when it yielded beautiful, needle-shaped crystals. It was afterwards found that the filtrate from the lead sulphide, on concentration and exposure to the air for a few days, also yielded the same crystals. After purification with alcohol and recrystallisation from water, the glucoside was obtained as a white, crystalline substance, m. p. 175—176°. The yield was about 0·6 per cent. of the weight of the dry leaves.

Capsularin is very bitter to the taste, and is sparingly soluble in water and insoluble in ether, but dissolves freely in alcohol

or acetone. It is neutral to litmus in aqueous solution, develops with sulphuric acid a beautiful red colour with green fluorescence, and is lævorotatory, having $[\alpha]_D$ −23·6° in ethyl-alcoholic solution (Found: in air-dried material, C = 59·52; H = 8·99; loss at 110—112° = 4·5. $C_{22}H_{36}O_8,H_2O$ requires C = 59·19; H = 8·5; H_2O = 4·0 per cent. Found: *in material dried at 110—112°*, C = 61·72; H = 8·68. $C_{22}H_{36}O_8$ requires C = 61·68; H = 8·41 per cent.).

A *penta-acetyl* derivative, prepared with acetic anhydride in the usual manner and crystallised from dilute alcohol, melted at 194° after being dried at 100° (Found: C = 59·69; H = 7·53; C_2H_3O [estimated by Perkin's method, T., 1905, **15**, 107) = 32·82. $C_{22}H_{31}O_8(C_2H_3O)_5$ requires C = 60·19; H = 7·2; C_2H_3O = 33·69 per cent.].

Hydrolysis of Capsularin.—The substance was heated under reflux for about four hours with 2 per cent. sulphuric acid, the white precipitate removed, and the filtrate, which reduced Fehling's solution, after treatment with barium carbonate and concentration to a small bulk in a vacuum, was warmed with phenylhydrazine hydrochloride and a few drops of glacial acetic acid, when an osazone was obtained. This, after crystallisation from dilute ethyl alcohol (1 : 1), melted, alone or admixed with *d*-glucosazone, at 203—204°. An aqueous solution of the sugar (about 3 grams in 40 c.c.) was optically inactive, but after treatment with yeast (free from any reducing or active sugar) for four or five days at room temperature it was found to be lævorotatory, showing that the sugar was a mixture of equal quantities of *d*- and *l*-glucose.

The second product of the hydrolysis, crystallised from 33 per cent. acetic acid, formed small needles melting at 185°. The substance is insoluble in water, but freely soluble in alcohol or ether, burns with a smoky flame, and gives with sulphuric acid a red colour with green fluorescence. It is insoluble in alkalis and does not reduce Fehling's solution, neither does it form any compound with phenylhydrazine. It reduces alkaline permanganate, and decolorises bromine in carbon tetrachloride solution (Found: C = 71·9; H = 10·19; *M*, in boiling ethyl alcohol, = 269. $C_{16}H_{26}O_3$ requires C = 72·18; H = 9·77 per cent.; *M* = 266).

The substance gave with acetic anhydride, chloroform, and concentrated sulphuric acid a violet colour changing to green, a reaction characteristic of the alcohols of the series $C_nH_{2n-6}O_4$ isolated by Power from the vegetable kingdom (T., 1908, **93**, 908; 1909, **95**, 249).

Repeated attempts to acetylate and benzoylate the second product of hydrolysis under different conditions met with no

success. When it was heated with phosphorus pentachloride in a water-bath, a yellow substance, probably a chloro-derivative, soluble in alcohol or ether, but insoluble in water, was obtained, which could not be induced to crystallise and therefore was not further examined.

The hydrolysis of the glucoside takes place in accordance with the equation $C_{22}H_{36}O_8 + H_2O = C_6H_{12}O_6 + C_{16}H_{26}O_3$.

The amount of glucose was estimated volumetrically with Fehling's solution (Found 41·82; calc., 42·05 per cent.) and the second product was extracted with ether, dried at 110—112°, and weighed (Found 62·63; calc., 62·15 per cent.).

Our grateful thanks are due to Babu Upendra Chandra Bhattacharja, M.A., who has kindly helped us in carrying out our polarimetric experiments.

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Dacca, Bengal. [*Received, February 20th*, 1922.]

CXXVI.—*The Rate of Evolution of Carbon Dioxide from Solution in Presence of Colloids.*

By Alexander Findlay and Owen Rhys Howell.

The rate at which a gas escapes from a supersaturated solution has been shown by Findlay and King (T., 1913, **103**, 1170; 1914, **105**, 1297) to be influenced by the presence of colloids. The method employed in investigating the process, however, involved a rather complicated arrangement of apparatus and considerable manipulative skill, and it seemed to be desirable to obtain some other and more simple method of studying the problem. We have therefore investigated the rate of desaturation of a solution of carbon dioxide when an indifferent gas is bubbled through the solution, the progress of de-aeration being followed by means of measurements of electrical conductivity (compare Perman, T., 1895, **67**, 868, 892; 1898, **73**, 511; Knox, *Ann. Physik*, 1895, **54**, 44; Meyer, *Z. Elektrochem.*, 1909, **15**, 249; Bohr, *Ann. Physik*, 1899, **68**, 500; Steele, T., 1903, **83**, 1470; Carlson, *J. Chim. Phys.*, 1911, **9**, 228). The method is essentially different from that employed by Findlay and King, and a precisely comparable behaviour is not to be looked for; but it is simple to carry out, and the results obtained, we believe, throw some further light on the behaviour of colloids.

Apparatus and Method.—The conductivity cell was a cylindrical

sel made of resistance glass, 12·5 cm. high and 3·4 cm. in diameter, ch could readily be connected with the gas inlet and outlet tubes means of glass tubes with tapered and ground ends.

The carbon dioxide used in the experiments was prepared by the ion of pure hydrochloric acid on white marble, and was washed by sage through solutions of potassium permanganate and sodium drogen carbonate, and then through distilled water. Before ering the conductivity cell, in which distilled water or water taining colloid was placed, the carbon dioxide was passed through fourth wash-bottle, placed in the thermostat and containing the me solution as the conductivity cell. In this way alteration of e concentration of the solution in the conductivity cell was oided.

For desaturation, a current of air was drawn at a constant rate rough the solution. The air was freed from carbon dioxide by assage through a long tube containing soda-lime, and then through wo wash-bottles containing potassium hydroxide and distilled ater, and lastly through a flask, immersed in the thermostat and ontaining a quantity of the solution used in the conductivity cell. Before entering the conductivity cell, the air was brought to the emperature of the thermostat by passage through about 8 feet of narrow copper tubing wound in spiral form and immersed in the thermostat. This precaution was found to be necessary in order to prevent the cooling of the solution by the stream of air.

All measurements were carried out at 25°. Fifty c.c. of the solution were introduced into the conductivity cell and its conductivity was determined. It was then saturated with carbon dioxide and the conductivity again determined. Air was aspirated through the solution and the conductivity determined every half-minute.

Calculation of Results.—As each air-bubble enters the solution the carbon dioxide diffuses into it at a rate which may be represented by the expression $-\frac{dC}{dt}=\frac{\Delta \cdot s}{l}(C_1-C_2)$, where Δ is a diffusion coefficient (*see later*), s the area of the surface of the bubble, l the thickness of the surface layer, C_1 and C_2 the concentration of carbon dioxide in the solution and in the bubble, respectively. If the bubbles pass through the solution at a constant and sufficiently rapid rate, the area, s, may be regarded as constant, and the concentration C_2 as zero. We may therefore write, since $\Delta \cdot s/l$ is constant for a given solution, $-dC/dt = kC_t$ where C_t is the concentration of the carbon dioxide in the solution at any time t. On integration, this yields the expression $k=\frac{1}{t}\log_e C/C_t$. In the case of weak acids, the conductivity, κ, is approximately proportional

to the square root of the concentration, expressed in gram-equivalents per litre, and we may therefore write $k = \frac{1}{t} \log_e \kappa^2/\kappa_t^2$.

The conductivities of the solutions of carbon dioxide were corrected by subtracting the conductivity of the water (in the case of pure aqueous solutions), or of the colloidal sol employed. The velocity coefficient was then calculated from these corrected values.

EXPERIMENTAL.

1. *Pure Aqueous Solutions of Carbon Dioxide.*—As the result of a large number of experiments, it was found that the desaturation of a pure aqueous solution of carbon dioxide proceeds in the same manner irrespective of the rate at which the current of air is passed. The rate of desaturation increases, it is true, with increase in the rate of passage of the air, but for a given rate the velocity coefficient remains practically constant until desaturation is nearly complete. In all our final measurements, therefore, a constant rate of air current was maintained. In Table I are given the results of one out of the many determinations of the velocity of desaturation of an aqueous solution of carbon dioxide. In this table, t represents time in minutes, κ the conductivity of the solution, κ_c the corrected conductivity obtained by subtracting the conductivity of the water from the conductivity of the solution of carbon dioxide, and k is the velocity coefficient.

TABLE I.

Conductivity of water, 2×10^{-6} reciprocal ohms.

t.	$\kappa_c \times 10^6$.	$\kappa_c^2 \times 10^{12}$.	$0.43\,k$.	
0	47·10	2218		
0·5	41·96	1760	0·201	
1·0	37·88	1427	0·192	
2·0	30·41	924·7	0·190	
4·0	19·46	378·6	0·192	Mean = 0·195
6·0	12·35	152·5	0·194	
8·0	7·72	59·6	0·196	
10·0	4·75	22·56	0·199	

It was found, in agreement with the results obtained by Findlay and King (*loc. cit.*), that the velocity of desaturation was quite independent of the time during which the carbon dioxide had been kept in solution.

2. *Solutions containing Starch.*—In these experiments Kahlbaum's soluble starch was employed. The starch was repeatedly washed with alcohol and with water in order to remove any soluble salts present. The solutions were prepared by adding boiling conductivity water to starch paste, and the mixture was then warmed on the water-bath for ten minutes, when it became clear. Starch

lutions of different concentration were employed, and it was found iat the rate of desaturation of solutions of carbon dioxide in presence : starch is considerably greater than in the case of pure aqueous lutions, and that it increases somewhat, although not markedly, s desaturation proceeds. This behaviour was found with all the tarch solutions investigated, and is more pronounced the greater he concentration of the starch. Even when the process of satura-ion and desaturation was repeatedly carried out with the same tarch solution, there was no change in the general behaviour of he solutions. The results obtained with starch solutions of lifferent concentration were as follow:

(*a*) One per cent. solution of starch; initial conductivity, 24·40 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·292 (extreme values = 0·289 and 0·314).

(*b*) 2·5 Per cent. solution of starch; initial conductivity, 56·10 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·338 (extreme values = 0·289 and 0·402).

3. *Solutions containing Dextrin.*—Kahlbaum's dextrin was used and was purified by dialysing an 8 per cent. solution for about a week against conductivity water, a little toluene being added to prevent the growth of moulds. The results given in (*c*), (*d*), and (*e*) are selected from a large number of determinations, all of which gave similar values:

(*c*) 1·64 Per cent. solution of dextrin; initial conductivity, 27·55 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·256 (extreme values = 0·242 and 0·278).

(*d*) 3·28 Per cent. solution of dextrin; initial conductivity, 48·81 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·242 (extreme values = 0·232 and 0·245).

(*e*) 6·56 Per cent. solution of dextrin; initial conductivity, 83·92 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·216 (extreme values = 0·217 and 0·226).

4. *Solutions containing Gelatin.*—French sheet gelatin was used. Before use it was cut up into small pieces and allowed to soak for several days in repeatedly changed conductivity water. Owing to the excessive frothing which took place during desaturation of the carbon dioxide solutions, only dilute solutions of gelatin could be employed. The results given in (*f*) are typical of those obtained in other cases:

(*f*) 0·25 Per cent. solution of gelatin; initial conductivity, 18·20 $\times 10^{-6}$ reciprocal ohms. $0·43k$: mean value = 0·117 (extreme values = 0·069 and 0·119).

5. *Solutions containing Ferric Hydroxide.*—A dialysed sol o ferric hydroxide was employed. A large number of determination

have been made, and the results given in (*g*) and (*h*) are representative of all:

(*g*) 0·69 Per cent. solution of ferric hydroxide; initial conductivity, $321 \cdot 1 \times 10^{-6}$ reciprocal ohms. $0 \cdot 43k$: mean value = 0·155 (extreme values = 0·130 and 0·153; maximum value = 0·174).

(*h*) 1·39 Per cent. solution of ferric hydroxide; initial conductivity, $510 \cdot 2 \times 10^{-6}$ reciprocal ohms. $0 \cdot 43k$: mean value = 0·192 (extreme values = 0·166 and 0·162; maximum value = 0·222).

Discussion.

When one considers the results detailed above, it will be observed that the presence of a colloid has a distinct influence on the rate of desaturation of a solution by the bubbling method. In the case of solutions of starch and of dextrin, the velocity coefficient of desaturation is greater, and in the case of ferric hydroxide and of gelatin, the velocity coefficient is smaller than that of pure aqueous solutions of carbon dioxide. As a rule, also, in the case of the colloid sols the values of the velocity coefficient are less constant than in the case of pure aqueous solutions, and generally show a trend towards increasing values as the desaturation proceeds. This increase in the velocity coefficient, which is specially marked in the case of gelatin solutions, may perhaps find its explanation in the changes which the colloid undergoes under the influence of carbon dioxide, and in consequent changes of surface tension of the solutions.

Although the values of the velocity coefficient show a definite trend, we have, for the purpose of comparison, taken the mean of the values, as indicated in Table I and in (*a*)—(*h*). These values we have collected together in Table II, column 2.

TABLE II.

Velocity coefficients of desaturation of solutions of carbon dioxide.

Solvent.		0·43 *k*.	Velocity coefficient (Findlay and King).
1. Starch solution,	1 per cent.	0·292	
,, ,,	2·5 ,, ,,	0·338	(3 per cent.) 0·037
2. Dextrin solution,	1·64 ,, ,,	0·256	
,, ,,	3·28 ,, ,,	0·244	(3 ,, ,,) 0·057
,, ,,	6·56 ,, ,,	0·216	
3. Water		0·195	0·065
4. Ferric hydroxide solution,	0·69 ,, ,,	0·154	
,, ,, ,,	1·39 ,, ,,	0·192	(1·35 ,, ,,) 0·067
5. Gelatin solution,	0·25 ,, ,,	0·117	(0·05 ,, ,,) 0·150

To find an explanation of the varying values of the velocity coefficient of desaturation by the bubbling method, we must consider the expression used in calculating these values (p. 1047). This expression involves the factor $\Delta . s/l$, where Δ represents a diffusion coeffi-

nt of carbon dioxide across the boundary layer between solution d air bubble, or, perhaps, we ought more correctly to say that represents the coefficient of evolution or escape of the gas from e boundary surface of the solution into the air bubble. It would em that we are dealing here, not with a true diffusion coefficient a gas across a film, for in that case we should expect that the value Δ and therefore the value of the velocity coefficient of desatura-on would be greatest in the case of the solution in which carbon oxide is most soluble (compare Exner, *Sitzungsber. Akad. Wiss. Vien*, 1874, **70**, ii, 465; Wiesner and Molisch, *ibid.*, 1889, **98**, i, 70). This, however, is not the case, for addition of gelatin raises e solvent power of water for carbon dioxide, and addition of starch nd of dextrin diminishes the solvent power (Findlay and Creighton, ., 1910, **97**, 536).

We come back, therefore, to the question, What is the property f the solution which determines the value of Δ and therefore the alue of the velocity coefficient of desaturation? It was suggested y Findlay and King (T., 1913, **103**, 1170) that the velocity of volution of carbon dioxide from supersaturated solution on being igorously shaken might be brought into relation with the surface ension of the solution, and that the lower the surface tension the more rapid would be the evolution of the gas. In the case of Findlay and King's experiments, this conclusion seems to be borne out, as a glance at column 3 of Table II will show; for starch and dextrin raise the surface tension of water, whereas gelatin lowers the surface tension. In our experiments, however, we find the inverse relationship between velocity of desaturation and surface tension of the solution; the velocity coefficient of desaturation varies synbatically, not antibatically, with the surface tension.

Since substances which lower the surface tension of a liquid become concentrated in the surface layer, we might regard the colloid as exercising a sort of blocking action and in this way retarding the escape of carbon dioxide from the solution. This explanation, however, would scarcely hold in the case of those colloids which, like starch, raise the surface tension of water, and for which the velocity of desaturation is greater than for water. We are inclined to believe, therefore, that it is not the surface tension of the solution which determines the rate of escape of a gas, but rather the internal pressure of the solution which varies synbatically with the surface tension. Determinations of the rate of desaturation of a gas solution by the bubbling method would therefore give a measure of the internal pressure of the solution. It will be of interest to find whether this is true for solutions of carbon dioxide in different, non-colloidal solvents.

It may also be pointed out that since it has been found (Skirrow, *Z. physikal. Chem.*, 1902, **41**, 139; Christoff, *ibid.*, 1905, **53**, 321; **55**, 622) that solvent power for a gas varies antibatically with the surface tension, we shall expect that the velocity coefficients of desaturation by the bubbling method will vary antibatically with the solvent power of the solutions for carbon dioxide. As indicated above, this has been found to be the case.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF ABERDEEN. [*Received, February 3rd*, 1922.]

CXXVII.—*The Sulphilimines, a New Class of Organic Compounds containing Quadrivalent Sulphur.*

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

PROFESSOR H. S. RAPER, of the University of Leeds, in a report to the Chemical Warfare Department dated May, 1917, showed that ββ′-dichlorodiethyl sulphide readily undergoes condensation with sodium toluene-*p*-sulphonchloroamide, $C_6H_4Me{\cdot}SO_2Na{:}NCl,3H_2O$, first described by Chattaway (T., 1905, **87**, 153) and now widely used as a germicide under the name of "chloramine T" (Dakin, Cohen, Dufresne, and Kenyon, *Proc. Roy. Soc.*, 1916, [*B*], **89**, 232). The manufacture of chloramine T has been recently described by Inglis (*J. Soc. Chem. Ind.*, 1918, **37**, 288T). The condensation product, of which the composition corresponds with the constitution $C_6H_4Me{\cdot}SO_2{\cdot}N{:}S(CH_2{\cdot}CH_2Cl)_2$, is highly crystalline, melts at 144·5°, and has been found useful for the characterisation of ββ′-dichlorodiethyl sulphide. We are indebted to Professor Raper for permission to examine further the reaction involved, which proves to be of very general application.

During the formation of the condensation product the bivalent sulphur atom of the organic sulphide becomes quadrivalent and a novel element of constitution is produced; it is suggested that the name "sulphilimine" should be given to the grouping $>S{:}NH$. We have been able to prepare sulphilimines from several alkyl sulphides as well as from ββ′-dichlorodiethyl sulphide; we have not been able to prepare such compounds from the tri-, tetra-, and hexa-chlorodiethyl sulphides recently described (this vol., p. 594). It thus appears that the more highly chlorinated diethyl sulphides are too feebly basic to yield quadrivalent sulphur compounds with the acidic toluenesulphonamido-group; in these attempts only toluenesulphonamide could be isolated. Triphenylarsine, however, condenses with chloramine T, yielding a double

ompound of the substance $C_6H_4Me{\cdot}SO_2{\cdot}N{:}As(C_6H_5)_3$ with *p*-toluene-ulphonamide; this reaction is in some respects analogous to that y which Staudinger and Hauser obtained triphenylphosphine-enzoylimine, $(C_6H_5)_3P{:}N{\cdot}CO{\cdot}C_6H_5$ (*Helv. Chim. Acta*, 1921, **4**, 861).

Experimental.

Methylethylsulphine-p-*toluenesulphonylimine*,

$MeEtS{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.

—On shaking methyl ethyl sulphide (3 grams) with a cold concentrated aqueous solution of chloramine T (10 grams), considerable evolution of heat occurs and a white, crystalline solid separates; after remaining for an hour, filtering, washing with cold water, and drying, a product (6·3 grams) is obtained which crystallises from hot benzene solution in fine, white needles melting at 133° (corr.) (Found: C = 49·1; H = 6·2; N = 5·9. $C_{10}H_{15}O_2NS_2$ requires C = 48·9; H = 6·2; N = 5·7 per cent.).

Diethylsulphine-p-*toluenesulphonylimine*, $Et_2S{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.—Diethyl sulphide (5 grams) is shaken with a cold dilute aqueous solution of chloramine T (14 grams) and the product (12·3 grams), obtained as above, dissolved in chloroform; on evaporation, the chloroform solution deposits crystalline material which, after washing with ether and recrystallisation from benzene, yields the condensation product in small, white, crystalline plates melting at 144° (corr.). Owing to the considerable heat evolution, it is desirable to work in dilute solution (Found: C = 51·0; H = 6·5; N = 5·3. $C_{11}H_{17}O_2NS_2$ requires C = 50·9; H = 6·6; N = 5·4 per cent.).

Both the above compounds are very soluble in chloroform, moderately soluble in cold alcohol, and almost insoluble in cold benzene; they are practically insoluble in hot ether or light petroleum.

ββ′-*Dichlorodiethylsulphine*-p-*toluenesulphonylimine*,

$(CH_2Cl{\cdot}CH_2)_2S{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.

—ββ′-Dichlorodiethyl sulphide (17·1 grams) is shaken with an aqueous solution of chloramine T (28 grams), when the condensation product immediately begins to crystallise; after an hour, the product is filtered off, washed with water, dried, and washed with light petroleum. On crystallisation from hot alcohol, the colourless material (33 grams) thus obtained yields the pure substance (23·5 grams) in the form of fine, white needles melting at 144·5° (corr.) (Found: C = 40·2; H = 4·7; N = 4·4. $C_{11}H_{15}O_2NCl_2S_2$ requires C = 40·2; H = 4·6; N = 4·3 per cent.).

Dibenzylsulphine-p-*toluenesulphonylimine*,

$(C_6H_5{\cdot}CH_2)_2S{:}N{\cdot}SO_2{\cdot}C_6H_4Me$.

—Dibenzyl sulphide (4·3 grams) is dissolved in acetone and well

shaken with a cold aqueous solution of chloramine T (6 grams); the condensation is completed by heating on the water-bath at 50° for a few minutes, when a crystalline solid separates. After diluting with water, evaporating off the acetone, and cooling, the crystalline material is filtered, washed, dried, and crystallised from hot benzene; it separates in white needles (5·8 grams) melting at 193° (corr.) (Found: C = 65·7; H = 5·5; N = 3·5. $C_{21}H_{21}O_2NS_2$ requires C = 65·7; H = 5·5; N = 3·6 per cent.).

On hydrolysing the four substances described above by boiling with water or dilute hydrochloric acid, *p*-toluenesulphonamide was obtained; no crystalline product corresponding with the sulphoxide of the alkyl sulphide was isolated.

*Diethyldisulphine-(bis)-*p*-toluenesulphonylimine*,

$$C_6H_4Me\cdot SO_2\cdot N\!:\!S{<}{\scriptstyle CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}S\!:\!N\cdot SO_2\cdot C_6H_4Me.$$

—An alcoholic solution of diethylene disulphide (2 grams) and chloramine T (8·5 grams) is boiled under reflux for an hour and cooled, the white solid (3·4 grams) which separates being then washed with water and dried. The product is insoluble in ordinary solvents, but dissolves in warm aniline and nitrobenzene; it is purified by repeated extraction with boiling chloroform and recovered as a white powder on evaporating the chloroform solution to a small bulk. The compound has no definite melting point, but commences to darken at 165°; decomposition is complete at 200° (Found: C = 47·4; H = 4·5; N = 6·1. $C_{18}H_{22}O_4N_2S_4$ requires C = 47·1; H = 4·8; N = 6·1 per cent.).

*Double Compound of Triphenylarsine-*p*-toluenesulphonylimine with* p-*Toluenesulphonamide*,

$$2C_6H_4Me\cdot SO_2\cdot N\!:\!As(C_6H_5)_3,C_6H_4Me\cdot SO_2\cdot NH_2.$$

—Triphenylarsine (3 grams) and chloramine T (6 grams) are boiled with water (300 c.c.), these proportions being necessary to give complete solution, and, on cooling, the pure condensation product (3·3 grams) separates in long, white needles; after washing with water and drying, the substance melts at 176·5° (corr.) and subsequent fractional crystallisation from boiling water, or extraction with boiling acetone, fails to alter the melting point and composition. Although the product is evidently a pure substance, analysis shows that it is not the expected triphenylarsylamino-*p*-sulphonyltoluene, but indicates it to consist of two molecules of this compound with one of *p*-toluenesulphonamide (Found: C = 58·6; H = 4·9; N = 3·7; S = 8·5; As = 13·4. $C_{52}H_{53}O_6N_3S_3As_2$ requires C = 61·0; H = 4·7; N = 3·7; S = 8·6; As = 13·4 per cent.). The analytical figures quoted are the means of a number of consistent results, but

it is obvious that the carbon determination is much too low; no explanation of this is suggested.

On boiling the substance with dilute hydrochloric acid and cooling, *p*-toluenesulphonamide separates and from the filtrate triphenylarsonium hydroxide, melting at 115°, is deposited on concentration; the identity of tbis substance was confirmed by preserving it for some time in a vacuum over phosphoric oxide, when it became converted into triphenylarsonium oxide melting at 187°.

It is noteworthy that no condensation product could be obtained by the action of chloramine T on either dimethylaniline or β-thiotolene.

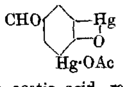
THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE. [*Received, May 4th*, 1922.]

CXXVIII.—*Mercury Compounds of Hydroxybenzaldehydes.*

By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP.

WHEN a solution of one of the three hydroxybenzaldehydes is boiled with mercuric acetate, mercury compounds are formed in which either one or two mercuric acetate residues, ·Hg·OAc, become attached to carbon atoms in the ring. The entry of these residues appears to be facilitated by the presence of the hydroxyl group, since benzaldehyde on similar treatment reduces the mercuric salt, the only crystalline substance so far isolated being mercurous acetate. Further, of the large number of organic compounds of mercury known none is derived from aromatic aldehydes except that recently prepared from vanillin by Paolini (*Gazzetta*, 1921, [ii], **51**, 188).

In the present paper, it is shown that with salicylaldehyde mercuric acetate residues are introduced at positions 3 and 5; with *p*-hydroxybenzaldehyde substitution presumably occurs at the same positions, but further action takes place between one of the ·Hg·OAc residues and the neighbouring hydroxyl group, with the loss of a molecule of acetic acid and the formation of the anhydro-substance represented by formula I.

(I.) 

This, on boiling with acetic acid, regenerates the normal 3:5-diacetoxydimercuri-4-hydroxybenzaldehyde. With *m*-hydroxy-

benzaldehyde, only one mercuric acetate residue is introduced, and its position has not yet been determined.

There is evidence also of the formation of a monomercurated derivative in the case of salicylaldehyde, but it has not so far been possible to obtain the substance in a pure state.

Mercury has been estimated in these compounds usually by destroying the organic matter with sulphuric acid and potassium permanganate and estimating the metal as sulphide, but in a few cases mercury, carbon, and hydrogen have been determined simultaneously by Abelmann's method (*Ber.*, 1914, **47**, 2935) and in others carbon has been estimated by Robinson's wet combustion method (T., 1916, **109**, 215).

Organic mercury compounds have acquired a new interest in recent years, owing to their increasing use in medicine, since they have the advantage over inorganic mercury compounds of not precipitating proteins, and of not being decomposed to any considerable extent by the metal of surgical instruments. Unfortunately, the utility of most of them is limited by their slight solubility in water, and this feature is shared by those now described. They yield sparingly soluble sodium salts, the bactericidal action of which is being examined by Major Brown, M.B., C.M., of the Wellcome Bureau of Scientific Research, who finds that *Bacillus typhosus* is killed in five minutes by solutions containing 0·034 and 0·002 per cent. of the ortho- and meta-compounds respectively, but only in twenty-five minutes by a solution containing 0·053 per cent. of the para-compound.

EXPERIMENTAL.

Preparation of the Mercury Compounds.—To one molecular proportion of the hydroxybenzaldehyde in a convenient quantity of 50 per cent. alcohol is added one or two molecular proportions of mercuric acetate dissolved in 50 per cent. alcohol containing 1 per cent. of acetic acid. This mixture is boiled under reflux until no more crystalline matter separates, when the flask is cooled and the mercury compound filtered off, washed with water, alcohol, and ether in succession, and dried. In the case of the meta-compound, no separation occurs until the reaction liquid has been concentrated. The compounds usually separate in a pure state, but they can be crystallised, if necessary, from hot acetic acid, or in the case of the meta-compound from alcohol containing 5 per cent. of acetic acid.

Derivatives of Salicylaldehyde.

3 : 5-Diacetoxydimercurisalicylaldehyde.—This substance, obtained as described, in a yield of 68·5 per cent. of the theoretical, forms a

ourless, crystalline powder consisting of minute, distorted cubes d melts at 133° (corr.) with decomposition. It is insoluble in st solvents, but dissolves in hot acetic acid and sparingly in etal; with sulphuric acid it gives an orange coloration [Found : = 20·01, 20·04; H = 1·92, 1·77; Hg = 62·6. $C_{11}H_{10}O_6Hg_2$ 39·2) requires C = 20·65; H = 1·56; Hg = 62·76 per cent.].

The substance dissolves in sodium hydroxide solution, forming a utral yellow liquid from which carbon dioxide causes the separa-on of a yellow precipitate of 3 : *5-dihydroxydimercurisalicylaldehyde*, hich darkens on heating, but does not melt up to 300° ound: Hg = 72·66. $C_7H_6O_4Hg_2$ (555·2) requires Hg = 72·24 r cent.].

Dilute hydrochloric acid added to a solution of the sodium salt uses precipitation of *3 : 5-dichlorodimercurisalicylaldehyde*, which arkens at 260°, sinters at 270°, but does not melt up to 310° [Found : Ig = 67·75 per cent. $C_7H_4O_2Cl_2Hg_2$ (592·1) requires Hg = 67·74 er cent.].

On shaking the finely powdered diacetoxy-derivative with excess f a 10 per cent. solution of iodine in potassium iodide, it is almost mmediately replaced by a yellow precipitate, which on recrystallisa-ion from methyl alcohol melts at 107·5° (corr.) [Found : C = 22·69; H = 1·17; I = 67·79. $C_7H_4O_2I_2$ (373·8) requires C = 22·48; H = 1·07; I = 67·90 per cent.].

This di-iodo-compound is identical with 3 : 5-di-iodosalicylaldehyde prepared by Seidel (*J. pr. Chem.*, 1899, [ii], **59**, 114) by the action of iodine on salicylaldehyde in presence of mercuric oxide. A specimen thus prepared melted at 107·5° and showed no depression of melting point on admixture with the di-iodo-derivative prepared from diacetoxydimercurisalicylaldehyde. The phenylhydrazone crystallises in yellow needles and melts at 172·5—173·5° (corr.). On oxidation with permanganate in acetone, the di-iodosalicylaldehyde is converted into 3 : 5-di-iodosalicylic acid, m. p. 225° (decomp.; corr.) [Found : I = 65·73. $C_7H_4O_3I_2$ (389·8) requires I = 65·1 per cent.].

The mercury compound formed from salicylaldehyde must therefore be 3 : 5-diacetoxydimercuri-2-hydroxybenzaldehyde.

The mother-liquor, which contains no free mercuric acetate, since it gave no precipitate with solution of sodium hydroxide or ammonium sulphide, was then poured into brine, when a voluminous, white precipitate formed, which, after washing with water, alcohol, and ether, and drying, contained 64 per cent. of mercury, and appeared to be a mixture of chloromercuri- and dichlorodimercuri-salicylaldehydes: it was insoluble in the usual solvents, but on extraction with hot acetal there remained undissolved a pale pink, amorphous

powder, which proved to be 3 : 5-dichlorodimercurisalicylaldehyde (see above) [Found : Hg = 67·47. $C_7H_4O_2Cl_2Hg_2$ (592·1) requires Hg = 67·74 per cent.]. The acetal solution on cooling deposited a pink solid which contained 58 per cent. of mercury instead of 53·4 required for a monochloromercuri-compound, and so far the latter has not been obtained in a pure state. Reduction of the amount of mercuric acetate used in the initial reaction to one molecular proportion merely reduced the ratio of pure diacetoxy-compound to mixed chloro-compounds formed from 8 to 1 to 0·8 to 1.

p-Hydroxybenzaldehyde.

The *p*-hydroxybenzaldehyde used was prepared by the method described in British Patent 161679, depending on the condensation of phenol with formaldehyde; a yield of 42·6 per cent. of the theoretical was obtained.

4 : 5-*Anhydro*-3-*acetoxymercuri*-5-*hydroxymercuri*-4-*hydroxybenzaldehyde* (Formula I).—This substance results as already stated (p. 1055) from the application of the general method to *p*-hydroxybenzaldehyde.

It occurs as a colourless, crystalline powder, which under the microscope is seen to be composed of masses of minute cubes, is insoluble in water and most organic solvents, and has no definite melting point [Found : C = 18·79, 18·31; H = 1·44, 1·47; Hg = 69·15. $C_9H_6O_4Hg_2$ (579·2) requires C = 18·64; H = 1·03; Hg = 69·24 per cent.].

On steam distillation, after decomposition by phosphoric acid, it yields 9·61 per cent. of acetic acid ($C_9H_6O_4Hg_2$ requires acetic acid = 10·36 per cent.). Hot acetic acid dissolves this anhydro-substance, converting it into 3 : 5-*diacetoxydimercuri*-4-*hydroxybenzaldehyde*, which separates as the solution cools in minute, colourless, glistening plates. This, like the anhydro-compound, darkens on heating but has no melting point up to 300° [Found : C = 20·74; Hg = 63·02. $C_{11}H_{10}O_6Hg_2$ (639·2) requires C = 20·65; Hg = 62·76 per cent.].

The diacetoxy-compound dissolves with difficulty in sodium hydroxide solution, yielding a slightly turbid solution, which could not be filtered clear. It is decomposed by carbon dioxide, yielding a dull grey precipitate of 3 : 5-*dihydroxydimercuri*-4-*hydroxybenzaldehyde* [Found : Hg = 73·07. $C_7H_6O_4Hg_2$ (555·2) requires Hg = 72·24 per cent.], and by hydrochloric acid, giving the corresponding *dichlorodimercuri*-compound [Found : Hg = 67·07. $C_7H_4O_2Cl_2Hg_2$ (592·1) requires Hg = 67·74 per cent.].

On shaking the finely-ground anhydro-compound with excess of iodine dissolved in potassium iodide solution, a pale yellow substance

obtained, which after crystallisation from alcohol forms colourless needles melting at 206·5° (decomp.; corr.). More of this substance can be isolated by removing the excess of iodine from the mother-liquor and acidifying with hydrochloric acid (Found: C = 22·41; H = 1·91; I = 67·75. Calc. for $C_7H_4O_2I_2$; C = 22·48; H = 1·07; I = 67·90 per cent.).

This di-iodo-compound is identical with the 3 : 5-di-iodo-4-hydroxybenzaldehyde prepared by Paal (*Ber.*, 1895, **28**, 2412) and shows no depression of melting point on admixture with a specimen made by Paal's method, although this author gives a lower melting point, 198—199°, than that now found. On oxidation with permanganate in alkaline solution the di-iodo-compound, prepared by either method, is converted into 3 : 5-di-iodo-4-hydroxybenzoic acid, which, however, melts at 261° (decomp.; corr.) instead of at 237° as recorded by Paal (*loc. cit.*). The authors find that by varying the rate of heating the melting point can be varied from 248° to 261°.

The mercury compound first formed from *p*-hydroxybenzaldehyde must therefore have the two mercury residues in positions 3 and 5, and since it yields only 1 molecule of acetic acid on distillation with phosphoric acid it must be 4 : 5-anhydro-3-acetoxymercuri-5-hydroxymercuri-4-hydroxybenzaldehyde (formula I).

m-*Hydroxybenzaldehyde.*

Acetoxymercuri-m-*hydroxybenzaldehyde*,

$$CH_3{\cdot}CO{\cdot}O{\cdot}Hg{\cdot}C_6H_3(OH){\cdot}CHO.$$

—This substance, obtained in almost quantitative yield by the general method (p. 1056), is much more soluble than the mercury derivatives already described and can be obtained only by concentrating the reaction liquid. It crystallises from acetic acid in colourless needles, m. p. 185—186° (corr.; decomp.), dissolves in solution of sodium hydroxide, forming a yellow liquid, and is coloured yellow by sulphuric acid [Found: C = 27·70, 27·78; H = 2·47, 2·55; Hg = 52·89. $C_9H_8O_4Hg$ (380·6) requires C = 28·38; H = 2·1; Hg = 52·70 per cent.].

It is decomposed by iodine in potassium iodide solution, yielding an *iodo*-m-*hydroxybenzaldehyde* [Found: I = 51·77. Calc. for $C_7H_5O_2I$ (247·9) I = 51·19 per cent.], which crystallises in yellow needles from dilute alcohol (15 per cent.), melts at 159—160°, and has powerful sternutatory properties.

On oxidation with permanganate in acetone it yields an *iodo*-m-*hydroxybenzoic acid*, melting above 233° to a cloudy liquid; this is not identical with 6-iodo-3-hydroxybenzoic acid (Limpricht, *Annalen*, 1891, **263**, 234), the only mono-iodo-derivative of

m-hydroxybenzoic acid so far known, and its constitution is being investigated.

The authors desire to express their thanks to Mr. F. P. Walton for assistance with the analytical work recorded in the paper.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

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CXXIX.—*The Constitution of Polysaccharides. Part IV. Inulin.*

By JAMES COLQUHOUN IRVINE, ETTIE STEWART STEELE, and MARY ISOBEL SHANNON.

IN the introduction to Part I of this series (Irvine and Steele, T., 1920, **117**, 1474), we took objection to the fact that other workers are now endeavouring to enter the field of research which has been developed in this laboratory during the past twenty years. It is unfortunately necessary to refer again to this matter in more direct terms.

As is well known, the majority of the investigations conducted here since 1901 have had as their main object the solving, by one particular method, of the constitutional problems of the carbohydrates. This programme of work has been clearly defined on several occasions, and the experimental methods employed have also been fully described. It is needless again to elaborate the principles involved in our structural studies, beyond stating that it is generally possible to replace the free hydroxyl groups in a carbohydrate by stable methoxyl groups, and that subsequent hydrolysis yields a methylated sugar or sugars. The identification of the scission products and of the position in them occupied by the alkyl groups supplies direct evidence as to the constitution of the parent complex.

For the success of such a scheme the main essentials are : (1) The development of methods for methylating carbohydrates without producing radical alterations in structure; (2) the preparation of a series of definite methylated sugars likely to be encountered in the hydrolytic products obtained from alkylated glucosides, disaccharides, and polysaccharides; (3) the determination of the constitution of these sugars, including the position occupied by the methyl groups and the nature of the oxygen ring present.

These necessary factors have been supplied in the course of the systematic investigations carried out in the St. Andrews

·atories. It will be recognised that the most fundamental incidentally the most difficult) aspect of such work is the y of the methylated hexoses and pentoses, which, as reference pounds, play a necessary part in the general scheme. With tice and patience, the conversion of a di- or poly-saccharide a methylated derivative becomes a comparatively simple ter; the hydrolysis of the methylated compounds and the ıtion of the sugars then formed are likewise simple processes if products are already known and their properties have been ɔribed. But the interpretation of the results and the permanent ue of such investigations depend on the constitution of the simple thylated sugars ultimately isolated. Recognising this fact, the rk of this laboratory was directed for many years to the study typical methylated aldoses and ketoses as a necessary preliminary the extension of our researches to the more attractive constutional problems presented by the complex carbohydrates. So ·, nineteen definite methylated monosaccharides have been epared and described for this purpose, and it need scarcely be marked that it was far from our intention to provide this informaɔn in order that others might forestall our programme by the use our methods and results. So long as we do not abandon this ıe of work it will be generally agreed that, in the interests of the ıbject, its development should remain in the laboratory where it as initiated.

Practically without exception, chemists have duly respected this ɔservation, but the series of papers dealing with our topics which as been published by Karrer and his pupils makes it necessary for ıs to give expression to our dissent and to review the situation ɔriefly. Reference is now made to a selection of our papers, vhich, it may be remarked, have appeared in steady succession ɔven during the years when we were engaged on national service.

The first account of methylation in the sugar group (apart from the production of methylglucosides) was given by Purdie and Irvine to the British Association in 1902 and, in a subsequent paper (T., 1903, **83**, 1026), these authors described the crystalline variety of tetramethyl glucose, incidentally confirming the butylene-oxide structure of the α- and β-methylglucosides. They also applied the methylation process to sucrose, and thus established the constitution of this disaccharide so far as the glucose half of the molecule is concerned. In the closing paragraph of the paper, the authors reserved the extension of their work "to other members of the sugar group and to natural glucosides." Similarly, Irvine and Cameron (T., 1904, **85**, 1081), in describing the methylation of galactose, expressed the intention of applying their results to the

case of lactose, and Purdie and Irvine (T., 1905, **87**, 1025), in proving the glucosidic structure of both sucrose and maltose by means of the methylation method, stated that they intended "to pursue the subject."

In the following year, a full description of how the structure of a glucoside or glucosidic sugar can be determined by methylation and hydrolysis was contributed by Irvine and Rose (T., 1906, **89**, 814), who selected salicin as a typical natural glucoside and solved the constitution of this compound. Working on similar lines, Irvine and Gilmour (T., 1908, **92**, 1420) showed that the same principles can be applied to identify true glucosides, and a general review of the position which had then been reached was published by one of us (Irvine, "Über die Verwendung alkylierter Zucker zur Bestimmung der Konstitution von Disacchariden und Glucosiden," *Biochem. Z.*, 1909, **22**, 357).

The extension of the work of the laboratory to carbohydrates other than glucosides and disaccharides was commenced in 1910, and, thereafter, the methylation of cellulose was described by Denham and Woodhouse (T., 1913, **103**, 1735). Up to this stage the silver oxide method of alkylation had been uniformly employed for our purposes, but the above authors showed that, where the solubility of the carbohydrate under examination prohibits the use of methyl iodide, normal methylation can be effected by means of methyl sulphate and alkali. Considering the success which attended Denham's work, he naturally did not content himself to restrict its application to the solitary example of cellulose or to the mechanical preparation of methylated celluloses. He accordingly stated his "intention to continue the investigation of the progressive methylation of cellulose and to study the cleavage products obtainable from methylated celluloses." He continued: "Experiments conducted on lines similar to those described above have also been carried out by the authors on starch, the results showing that the starch molecule similarly undergoes normal methylation."

The methylation of polysaccharides for the purposes of structural investigations was thus definitely reserved for this laboratory as a natural extension of its programme, and the point was again emphasised at a later stage (Denham and Woodhouse, T., 1914, **105**, 2362) when crystalline trimethyl glucose was first isolated from trimethyl cellulose. It is also significant that, as a necessary step in the rational study of polysaccharides according to our methods, Irvine and Hogg at this stage examined monomethyl glucose for the stated reason that "incompletely methylated glucoses are likely to be encountered among the hydrolysis products of alkylated

ysaccharides" (T., 1914, **105**, 1380). The object of this orious work was thus clearly defined.

Nith regard to the constitution of disaccharides, the situation equally clear, as it has already been shown that our investigations re begun and our methods described so far back as 1903. A teworthy simplification of the experimental procedure was bsequently developed by Haworth, who, working in this oratory, applied the methyl sulphate method of alkylation to crose (T., 1915, **107**, 8). Of greater practical importance was s discovery that reducing sugars generally, including both monoccharides and disaccharides, when dissolved in alkali and treated th methyl sulphate, are converted in the first instance into the rresponding "methyl-glucosides," which afterwards undergo rther methylation in the sugar chain. As the older methods for e preparation of glucosides from disaccharides are extremely dious, this simplification proved of great service and facilitated e constitutional study of lactose, maltose, and cellobiose (Haworth nd Leitch, T., 1918, **113**, 188; 1919, **115**, 809; Haworth and lirst, T., 1921, **119**, 193). In each of the cases mentioned, complete ethylation of the sugar was effected by using the methyl sulphate eaction, either alone or in conjunction with the silver oxide eaction. Hydrolysis then yielded the corresponding methylated exoses, all of which had been previously prepared and examined ere, so that definite constitutions could at once be assigned to he parent disaccharides.

The account given above shows that our scheme has throughout een systematically pursued, and attention may now be directed o the nature of Karrer's recent publications. Two years ago, Karrer published a short note (*Helv. Chim. Acta*, 1920, **3**, 620) describing some preliminary experiments on the methylation of starch carried out ostensibly with the object of obtaining derivatives which would display true solubilities and thus permit of molecular weight determinations. No serious objection need be taken to this topic, but, by a sweeping generalisation, the author reserved the study of methylated starches in various directions. This comprehensive reservation would, of course, include the hydrolysis of methylated starches, and was made without any reference to our prior claims on this field or to Denham's work on the alkylation of starch. It is highly significant that no experimental or analytical details are given in Karrer's paper, which was obviously designed to secure priority.

In later publications, however (Karrer and Nägeli, *Helv. Chim. Acta*, 1921, **4**, 185, 678), further experiments on the methylation of starch are described. These papers disclose the fact that Karrer

is apparently unaware that the methylation of non-reducing saccharides without rupture of glucosidic linkages was first accomplished by one of us, but a more serious point is his attempt to claim novelty for the use of methyl sulphate and concentrated alkali as a methylating mixture applicable to carbohydrates. The statement is actually made that such reactions had hitherto been conducted only in weakly alkaline solution. Now, Denham and Woodhouse had for several years used 15—18 per cent. aqueous sodium hydroxide in the methylation of cellulose and had applied the same reagents to starch. Further, in the methylation of disaccharides by means of methyl sulphate, Haworth and his co-workers employed solutions of sodium hydroxide the strength of which was approximately 30 per cent. The expression "feebly alkaline" is vague, but can scarcely be applied to solutions of the concentration quoted above, particularly as the alkaline concentration used by Karrer and emphasised by him as an innovation was of the order 20 per cent. Finally, in completing his methylations, Karrer again follows our example and employs the silver oxide reaction.

In a similar fashion, by the use of methods exactly parallel or identical with our own, Karrer proceeded to the methylation of inulin, the paper describing his results (Karrer and Lang, *Helv. Chim. Acta*, 1921, **4**, 249) appearing after our first publication on this subject. Indirectly, he also appropriated our constitutional methods for the study of cellulose (Karrer and Widmer, *Helv. Chim. Acta*, 1921, **4**, 174). He did not repeat the methylation of cellulose, but after the very obvious statement that the constitution of this polysaccharide must be based on that of cellobiose, he continues : "we experimented by the methylation and hydrolysis of methyl-cellobioside, to obtain a view of its constitution."

In this way he secures entry into another section of our field, presumably finding justification in the implied originality of his methylation process. Here again the unwarranted claim is made that the method adopted for the direct conversion of cellobiose into its glucoside is new, in that "hitherto the methylation of disaccharides has always been carried ont in weak alkali." The statement is totally inaccurate. The direct formation of a glucoside from a reducing sugar, as developed by Haworth, involves, as already stated, the use of highly concentrated alkali, and Karrer simply adopted the same process without any essential modification. The paper under discussion is admittedly incomplete, but was followed by a second publication (Karrer and Widmer, *Helv. Chim. Acta*, 1921, **4**, 295), in which the constitution of cellobiose is determined from the structure of the methylated glucoses formed when hepta-

methyl methylcellobioside is hydrolysed. To achieve this result (which had already been published by Haworth and Hirst), Karrer again made use in succession of the methyl sulphate and silver oxide reactions, as described from this laboratory. Having identified the methylated glucoses, Karrer then proceeds to utilise the constitutions for these compounds as established in this laboratory and, in the end, does no more than confirm the constitution of cellobiose previously deduced from precisely the same evidence (see also Irvine and Soutar, T., 1920, **117**, 1496). It is needless to refer to other points which emerge in these papers, and a due appreciation of Karrer's attitude may safely be left to the judgment of chemists. It is unlikely that our reservations have been deliberately ignored by him, and perhaps the only conclusion to form is that the earlier papers from this laboratory have been overlooked.*

The present communication deals with inulin, which has already been shown by us (Irvine and Steele, *loc. cit.*) to consist of an aggregate of γ-fructose residues, each ketose molecule having lost two hydroxyl groups in the formation of the polysaccharide. This conclusion is based on the fact that inulin gives a trimethyl derivative which on hydrolysis yields a *dextro*-rotatory form of trimethyl fructose. This sugar, in turn, is convertible into tetramethyl

* In this connexion, the following additional evidence is instructive. Karrer and Weidmann (*Helv. Chim. Acta*, 1919, **2**, 260) imply that little is known of *N*-glucosides and describe their attempts to prepare *N*-glucosido-anthranilic acid by an elaborate method. Although a "moderately pure" ammonium salt was obtained, they were unable to isolate the corresponding acid and came to the conclusion that the compound must be extremely unstable and incapable of independent existence. The real position of affairs is that this interesting *N*-glucoside and several others of the same type had been prepared and fully described ten years before Karrer's unsuccessful attempts were recorded (see Irvine and Gilmour, T., 1909, **95**, 1553). In place of being difficult, the condensation of glucose with anthranilic acid proceeds smoothly at the ordinary temperature, and we afterwards applied the reaction to the preparation of similar *o*-carboxyanilides from galactose, rhamnose, mannose, and maltose (Irvine and Hynd, T., 1911, **99**, 161).

Attention may also be directed to another equally significant omission. Karrer (*Helv. Chim. Acta*, 1921, **4**, 130) explains the dual reaction of the silver salts of ortho-hydroxy-acids towards acetobromoglucose as due to the silver atom being coupled simultaneously to carboxyl and hydroxyl. No doubt this is correct, but Karrer claims that we have here the first exact evidence for the doubly-linked condition of the metal in the interior of complex salts. The statement is inaccurate. So far back as 1898, Purdie showed that the action of alkyl haloids on the silver salts of hydroxy-acids gave (1) the hydroxy-ester, (2) the alkyloxy-acid, and (3) the alkyloxy-ester (Purdie and Lander, T., 1898, **73**, 287 and subsequent papers). It was, in fact, the exploitation of this general reaction which led ultimately to the discovery of the silver oxide process of methylation now used by Karrer.

γ-fructose, so that the fructose residue in inulin is identical with that present in sucrose. Shortly after the appearance of our paper, Karrer and Lang (*Helv. Chim. Acta,* 1921, **4**, 249) also described the methylation of inulin, which they likewise effected by using the methyl sulphate and the silver oxide reactions in succession. No mention was made by these authors of the hydrolytic products obtainable from trimethyl inulin, and there are obvious reasons for this important omission. Beyond the determination of molecular weights, the only positive contribution in Karrer's paper is that inulin when subjected to our processes gives a trimethyl derivative, a result which we had already shown to be the case.

Despite the absence of any additional evidence regarding the structure of inulin, Karrer's paper contains a number of direct and implied criticisms of our work on this subject. These will be dealt with in due course, but as he focuses on two points they may now be discussed in detail. We claimed that the methylation of inulin, when conducted with methyl sulphate and alkali, shows a tendency to be arrested at the stage where a definite dimethyl inulin is the essential product. This statement, which has been confirmed, was originally made on the evidence supplied by three separate experiments in each of which 32 grams of the disaccharide were employed. It is impossible to say how often Karrer repeated the reaction, but the yields quoted by him suggest a single preparation involving initially only 10 grams of inulin and giving less than half this weight of a "methylo-inulin" (OMe = 39 per cent.). We were naturally aware of the fact that, during the first stages of alkylation, inulin gives a mixture of products, including some trimethyl inulin. Inspection of our experimental details shows, however, that any fully methylated compounds were removed in the course of isolating dimethyl inulin, and also that, unlike Karrer, we confirmed by means of combustion analyses the Zeisel determinations made on all the compounds.

To substantiate our former results, we have repeated the methylation of inulin, in quantities of 32 grams, on six separate occasions and have again established that, under the conditions described, dimethyl inulin is the essential and the only definite product in each case. The optical rotation ascribed to the compound has also been confirmed, the value in chloroform ranging from $[\alpha]_D - 42{\cdot}6^\circ$ to $-44{\cdot}8^\circ$, our former figure being $-42{\cdot}1^\circ$. This constancy in composition and physical properties is consistent with the idea that a definite compound exists, and the point is not unimportant.

On the other hand, Karrer's "methylo-inulin" is a mixture, but at all events it possessed the merit of containing less inorganic impurity than our earliest preparations of dimethyl inulin. Con-

sidering the ultimate object of our work, and that the interest attached to a methylated inulin lies in the study of the volatile hydrolysis products to which it gives rise, this is a matter of little importance. One of the chief advantages of our constitutional methods is that in cases where methylated carbohydrates cannot be crystallised and are not sufficiently volatile to be distilled, impurities are removed after hydrolysis. The sugars then formed are readily distilled and all mineral matter is thus eliminated. It is significant that Karrer was enabled to free his material from mineral salts by solution in ether. Our normal preparations of dimethyl inulin are practically insoluble in ether, as one would expect, although they dissolve in an ethereal solution of trimethyl inulin. This distinction between our preparations and Karrer's specimen at once suggests that, in the latter case, depolymerisation had occurred during methylation, thus increasing the solubility in organic solvents. Our experience has shown that alkylation of the polysaccharide is accompanied by curious and irregular fluctuations in solubility, which may be attributed to depolymerisation and polymerisation. The solubility of the product appears to be influenced by at least two factors, the extent of the substitution and the degree of molecular association. One striking example may be quoted. After subjecting inulin to two treatments with methyl sulphate, part of the product is readily soluble in boiling ether. The methoxyl content of the soluble portion is of the order 39 per cent., a value which is intermediate between that required for two and three alkyl groups for each C_6 unit. On completing the methylation by the silver oxide reaction, a process which in a monomolecular compound would further increase the solubility in ether, two distinct series of products were obtained, one freely soluble and the other insoluble in this solvent. Both sets of compounds were nevertheless identical in composition and may be described as trimethyl inulin, as each gave the same sugar (trimethyl γ-fructose) on hydrolysis.

Having established the accuracy of our observations on dimethyl inulin, we again directed our attention to the preparation of trimethyl inulin. On the previous occasions this was effected, as a matter of convenience, by Purdie's reaction, which was conducted in the usual manner for eight hours. Karrer adopted the same method, but introduced the extraordinary variation of continuing the reaction at the boiling point for a week. It is difficult to find any justification for this procedure, as it has long been known that the normal treatment of eight hours is sufficient to convert about 96 per cent. of the silver oxide into iodide (Purdie and Bridgett, T., 1903, **83**, 1038). The trimethyl inulin we originally obtained

was a viscous syrup which differed from Karrer's product in bei dextrorotatory. Although pronounced alterations in rotato power are not infrequently encountered in progressive methylatio we remarked at the time on this change of sign in converti dimethyl inulin into trimethyl inulin.

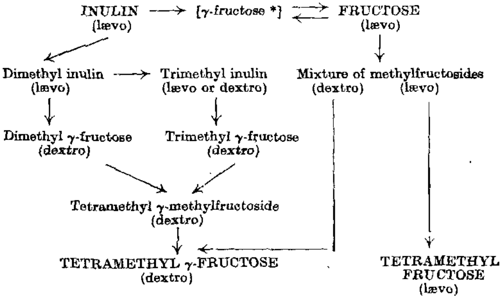
It has now been shown that the physical properties of trimeth inulin vary in marked degree according to the experimental pr cedure adopted in preparing the compound. Good reasons exi for ascribing this result to progressive depolymerisation occasione by several factors, which will be described in a subsequent pape Taking into account the elementary nature of the purificati possible with such compounds, we did not consider it advisable t test this view by molecular weight determinations, but a revie of the properties of different preparations of trimethyl inulin leav no doubt that the substance is readily depolymerised. The preparations varied from an amorphous solid, soluble in alcoh but insoluble in ether, to an extremely viscous soluble syrup whic after drying at 100°/70 mm., and subsequent cooling, may l described as a flexible glass. Other preparations displayed prope ties intermediate with the above, the average specimen being soli and readily soluble in ether. This gradation in solubility is accon panied by alterations in optical activity, the syrupy variety, a already described, being dextro-, and the solid amorphous forn lævo-rotatory. Irrespective of solubility or rotation, all th specimens summarised above possessed the composition of a full methylated inulin and gave on hydrolysis the same form of trimeth γ-fructose. In consequence, we have now shown that the læv rotatory varieties of trimethyl inulin undergo a change of sig during hydrolysis, whereas the dextrorotatory isomerides do no

In the meantime, it is premature to state definitely what con bination of factors is responsible for altering the condition molecular magnitude in the inulin series. Of seven preparatio of trimethyl inulin, two were dextro- and five were lævo-rotator The latter varieties were unaffected in rotation by fusion, by boilin in chloroform solution with charcoal, or by heating with alcoh or acetone. These processes are incidentally involved in isolatin the products when the final methylation of inulin is effected b the silver oxide reaction, yet nevertheless the dextro- forms we obtained when this reaction was frequently repeated. As a furth complication, which indicates sufficiently the difficulties involve reference may be made to the account of dimethyl inulin, where is shown that the silver oxide reaction appears to promote bot polymerisation and depolymerisation.

It is thus impossible to ascribe rigid properties to trimethyl inuli

and the description given by Karrer that the compound is an amorphous solid melting at 102—107° and showing $[\alpha]_D - 43°$ in chloroform solution applies to what is apparently a highly polymerised form of the compound, although his statement that it resembles the simple methylated sugars can only refer to methylated sugars unknown to us.

The extent of polymerisation and the magnitude of the optical activity of a fully methylated inulin do not, in the slightest degree, affect the validity of the views we formerly expressed regarding the structure of the polysaccharide. We find that all forms of trimethyl inulin, irrespective of their solubility or rotation, undergo hydrolysis to give the same dextro-trimethyl γ-fructose. Of greater significance is the further observation that dimethyl inulin, which so far has always been isolated as a lævorotatory compound, shows a change of sign on hydrolysis, owing to conversion into a *dextrorotatory dimethyl γ-fructose.* As will be seen from the outline of our results shown below, this is valuable confirmatory evidence as to the form of fructose of which inulin is a derivative. The scheme also emphasises that when inulin is converted into the ordinary variety of the ketose the change is not direct, but involves the preliminary formation of γ-fructose, which then undergoes structural rearrangement.



* "γ-Fructose" has never been isolated in the unsubstituted state, but *its properties may be deduced from those of its derivatives. The above* scheme postulates the existence of a dextrorotatory methylfructoside which has already been obtained in this laboratory by Dr. R. C. Menzies. Other results on the methylation of fructose embodied *in the scheme* may be found in Purdie and Paul (T., 1907, **91**, 289), Steele (T., 1918, **113**, 257), and Irvine and Robertson (T., 1916, **109**, 1305).

In view of the results now submitted and those already contributed, there is no need again to refer to our former generalisations on the structure of inulin beyond stating that apparently the arguments used by us have not been fully understood by our critics. The subject is admittedly difficult, but we showed conclusively that γ-fructose is the basis of inulin. Karrer, on the other hand, without producing any evidence for or against this view, maintains that whilst the polysaccharide is derived from an anhydro-sugar, it is impossible to say definitely which sugar it is. The caution thus displayed does not extend to his suggested distinction between starch and inulin, a problem which will be dealt with in a future paper from this laboratory. Meanwhile, however, we must refer briefly to his implication that, in our first communication, having proposed a structure for inulin, we subsequently withdraw it to a large extent. It is surely clear that we deduced merely a formula for the simplest possible unit present in inulin, and thereafter show how it may be expanded or modified. No other policy would have been justified even with the comprehensive data at our disposal. Our argument did not result, as he states, in " den alten langen Kettenformel," and the value of this criticism will be evident when it is observed that all our formulæ are based on a structure for γ-fructose. The existence of this variety of fructose was predicted as recently as 1916 hy Irvine and Robertson (*loc. cit.*), and the compound was first isolated, in the form of its tetramethyl derivative, by Haworth and Law (T., 1916, **109**, 1314). Until we did so, no one has suggested a formula of this nature for inulin, and the words quoted above cannot be applied to our structure, if to any. There is no need to refer in detail to Karrer's criticism of our claim that the soluble (and apparently depolymerised) trimethyl inulin may be distilled in a very high vacuum, as his statements do not agree with those made in our paper.

We do not propose to be diverted from our research programme or to adopt the method of publishing fragmentary results in frequent papers. Our researches are therefore being continued on inulin and other polysaccharides, including starch, glycogen, and cellulose. These and similar structural investigations on carbohydrates generally are in progress in this laboratory, and will be prosecuted with the utmost vigour. In view of the issues raised in this paper, it seems advisable to repeat once more that we are engaged in attempts to synthesise sucrose from the form of fructose which we have shown to be present in inulin.

Experimental.

Methylation of Inulin.—First Stage.

In repeating this preparation, the method described by Irvine and Steele was in the first instance followed exactly, using inulin from the same source and identical weights of the methylating reagents. The only difference observed was that the yield of dimethyl inulin was considerably less than that previously quoted, but this was traced to pronounced adsorption in the variety of charcoal used for decolorising purposes. In the subsequent preparations, the treatment with charcoal was either omitted or reduced to a minimum, and various minor alterations were introduced so as to eliminate oxidation. The following is an account of one typical experiment.

Thirty-two grams of finely-powdered inulin were dissolved in 60 c.c. of 30 per cent. sodium hydroxide solution at 60—70°, and the liquid was cooled to 35°. The solution was maintained at this temperature and kept in active motion by a mechanical stirrer whilst 80 c.c. of purified methyl sulphate and 200 c.c. of 35 per cent. aqueous sodium hydroxide were run in simultaneously, so that the alkali was always in excess. The addition of these reagents extended over three hours. With the exception that 92 per cent. alcohol was employed to precipitate the inorganic salts formed in the methylation, the further procedure up to the stage where two alkylations had been conducted was as described by Irvine and Steele.

The syrupy product thus obtained was dried in the vacuum oven at 100° until converted into a glass, which amounted to 73 per cent. of the weight of inulin used. After being finely ground with successive quantities of cold ether (free from alcohol), the undissolved material was extracted with the same solvent at the boiling point. The residue was then dissolved in chloroform and, if necessary, boiled for half an hour with decolorising charcoal. This solution was filtered, kept in contact with anhydrous potassium carbonate, the solvent evaporated, and the residue dried at 100° in a vacuum. In this way, dimethyl inulin was obtained as a white, amorphous solid.

Dimethyl Inulin.—It is to be noted that not only the yield, but apparently also the solubility, of dimethyl inulin is much affected by the quality of the decolorising charcoal used in its purification and by the duration of the boiling in chloroform solution. The maximum yield obtained was 77 per cent., but when specially adsorptive charcoal was employed this figure was diminished to

less than one-half. The results of one experiment are instructive: Thirty-two grams of inulin gave 24 grams of dimethyl inulin, but this weight was reduced to 6·7 grams after further boiling in chloroform solution with "anti-gas" charcoal. Not only so, but the bulk of the material then recovered had acquired a ready solubility in ether, although the negative reaction towards Fehling's solution showed that this was not due to hydrolysis. A possible explanation of this change in solubility is given in the introduction, and our description of dimethyl inulin is thus restricted to the solid form of the compound which is practically insoluble in ether, but dissolves in alcohol, chloroform, or acetone.

The mean of three consistent analyses, conducted on the product of independent preparations, was C = 50·79; H = 7·30; OMe = 34·7. $[C_6H_8O_3(OMe)_2]_x$ requires C = 50·53; H = 7·37; OMe = 32·7 per cent. The rotations of the three corresponding specimens in chloroform solution were:

$[\alpha]_D^{20^\circ}$ − 44·8° for c = 1·845,
,, − 42·6° for c = 1·845,
,, − 44·9° for c = 1·703.

As Irvine and Steele quoted $[\alpha]_D$ − 42·1° for c = 1·845, there is no reason to depart from the statement that dimethyl inulin is a definite compound or to modify our previous account of the substance.

Treatment of the By-products Soluble in Ether.

In isolating dimethyl inulin from the crude product of methylation, part of the material dissolves in ether and is removed. These soluble products, which correspond in methoxyl content with Karrer's "methylo-inulin," varied considerably in amount, and on one occasion as much as 45 per cent. of the total material was found in the ether extract. The syrup isolated on removal of the solvent was converted into a glass when dried at 100°/70 mm., and different preparations gave discordant carbon and hydrogen values. On the other hand, the methoxyl content and the specific rotation in chloroform showed little variation. The extremes recorded were:

C = 50·9; H = 7·0; OMe = 39·7; $[\alpha]_D$ = − 46·3°.
C = 52·7; H = 7·5; OMe = 38·8; $[\alpha]_D$ = − 43·7°.

Although the whole of the material had originally been dissolved in ether, the solubility in this solvent was affected by thorough drying. On grinding the brittle mass with successive amounts of ether only a portion passed into the solution, which was filtered and

ated. The undissolved solid was thereafter dissolved in form and the solution filtered and evaporated. In each case, sidue thus obtained was dried in the vacuum oven at 100°. s treatment, the original mixture was approximately separated wo components showing practically the same methoxyl con- OMe = 41·6 and 40·4 per cent. respectively), but displaying a ence in the carbon values :

Residue from Ether.

C = 52·22, 52·11 ; H = 7·70, 7·66.

Residue from Chloroform.

C = 51·90, 51·59 ; H = 7·46, 7·52 per cent.

composition of the more soluble product (*a*) approximates to of a trimethyl inulin, but repetition of the treatment with r failed to improve the analytical figures. It is unlikely that er of the products just described is a mechanical mixture of and tri-methyl inulin, and they probably consist of methylated ins, in which some of the anhydro-fructose residues are fully hylated whilst others still contain one unsubstituted hydroxyl up.

Conversion of Lævo-dimethyl Inulin into Dextro-dimethyl γ-Fructose.

Owing to the sparing solubility of dimethyl inulin in aqueous alic acid, it was necessary, in order to obtain a polarimetric record the hydrolysis, to use aqueous alcohol as the solvent and to employ ute solutions. The course of the reaction is indicated by the sults of the following experiment, in which the solution was boiled der a condenser and readings taken every thirty minutes.

oncentration of dimethyl inulin . . . 0·5 per cent.
oncentration of oxalic acid . . . 0·3 per cent.
omposition of solvent . . . . 70 per cent. alcohol.

Time from start.	$[\alpha]_D^{15°}$.	Time from start.	$[\alpha]_D^{15°}$.
0	− 39·0°	3½ hours	Inactive
30 minutes	− 36·3	4 ,,	+ 6·0°
1 hour	− 32·9	5 ,,	+ 12·1
1½ hours	− 28·6	6 ,,	+ 15·6
2 ,,	− 21·6	8 ,,	+ 17·4
3 ,,	− 4·3	10 ,,	+ 18·2 (constant)

When the complete results are expressed graphically (specific rotation values plotted as ordinates and time in hours as abscissæ), a regular curve is obtained, the form of which in the initial period suggests that the hydrolysis takes place in stages. Having estab-

lished by means of three experiments the above optical inversion which accompanies the hydrolysis, 10 grams of dimethyl inulin were converted into dimethyl fructose under similar conditions.

A solution of the compound was prepared in absolute alcohol and sufficient aqueous oxalic acid added to give a system containing 70 per cent. of alcohol, 1 per cent. of acid, and 1·266 per cent. of dimethyl inulin. Even after repeated filtration, the liquid was faintly turbid during the early stages of the hydrolysis, which was conducted by boiling under a condenser. After seven hours, the rotation had altered from lævo to dextro, and had attained a constant value. The liquid was neutralised with calcium carbonate, filtered, treated with charcoal, and evaporated to dryness under diminished pressure. A syrupy residue remained which was extracted with boiling acetone, dried over sodium carbonate, and the solvent removed. Dimethyl γ-fructose was thus obtained as a thick syrup, which was dried at 60°/100 mm. Yield = 72 per cent.

Dimethyl γ-Fructose.

Although the sugar, isolated as described above, was perceptibly volatile when heated under highly diminished pressure, no attempt was made to purify the compound by distillation. This was avoided, as, in the absence of exact evidence as to the position of the hydroxyl groups, the possibility remained open that transformation to the butylene–oxide type might take place (Found: C = 46·19; H = 7·73; OMe = 30·42. $C_8H_{16}O_6$ requires C = 46·15; H = 7·69; OMe = 29·81 per cent.). $[\alpha]_D^{20°}$ in chloroform = + 17·1° for c = 2·675. As doubtless two stereoisomeric forms corresponding with the α- and β-configurations were present, the above optical value is only significant in so far as it proves that the sugar is derived from γ-fructose. Dimethyl γ-fructose dissolves freely in water, alcohol, or acetone. The aqueous solution reduces potassium permanganate instantly in the cold. Fehling's solution and ammoniacal silver nitrate solution are likewise reduced at the ordinary temperature, although more slowly. On the other hand, Schiff's reagent and mercuric chloride solution are unaffected. These properties are characteristic of γ-sugars, but to establish this point the dimethyl fructose was condensed with methyl alcohol to give the corresponding methylfructoside. This, in turn, was converted into tetramethyl methylfructoside, which on hydrolysis gave tetramethyl γ-fructose (see Irvine and Steele, *loc. cit.*, for experimental details of similar reactions). The composition, reducing properties, and physical constants of the sugar thus obtained were in good agreement with the standard values.

Trimethyl Inulin.

ıe conversion of dimethyl inulin into a soluble dextrorotatory ι of trimethyl inulin has already been described. Details of her similar preparation may now be given. The starting erial employed was a methylated inulin obtained after one tment with sodium hydroxide and methyl sulphate and, before her alkylation, the substance was extracted with boiling ether, methoxyl content of the residue being 27·5 per cent. An raneous solvent was thus necessary to effect complete solution continuing the methylation by the silver oxide reaction. The tomary procedure was followed, the total product after each ction being dried at 100°/20 mm.

First Methylation.—Substance, 25 grams; silver oxide, 63 grams; thyl iodide, 100 grams; methyl alcohol, 30 c.c. Duration of ıting, eight hours; extracting agent, methyl alcohol.

Second Methylation.—Duplicate with the above. Yield of pro-et 20 grams, of which 4 grams were soluble in ether and 16 grams uble in alcohol.

Third Methylation.—Duplicate with the above, save that no solvent cohol was required, a clear solution in methyl iodide being obtained ι the addition of a few drops of acetone. Acetone was also used the extracting agent. Yield 15 grams; OMe = 38·6 per cent.

Fourth Methylation.—No extraneous solvent was required in this ıse, and the alkylated product was freely soluble in ether, which as used as the extracting agent. Otherwise the conditions were ıe same as in the previous alkylations. Yield, 12 grams; Me = 42·4 per cent.

Fifth Methylation.—Duplicate with the fourth. Yield 10·5 grams. he product was a glass (Found: C = 52·9; H = 7·7; OMe = 44·3 er cent.). In chloroform solution, for $c = 2$, $[\alpha]_D^{20°} = +59·2°$. n hydrolysis with aqueous oxalic acid, 7·5 grams gave 6 grams of ure trimethyl γ-fructose. The original compound thus possesses he composition and properties of a *trimethyl* inulin.

Preparation of Two Isomeric Forms of Lævo-trimethyl Inulin.

We have found that the lævorotation of the methylated inulins is generally preserved when the silver oxide reaction is applied to material already methylated by methyl sulphate to an extent which renders the use of an extraneous solvent unnecessary and permits of the final alkylation being conducted in one operation. Even under these conditions, it was ascertained that the silver oxide reaction introduces factors which modify considerably the proper-ties of the trimethyl inulin produced. This is clearly shown by

considering the effect of methylation on the soluble products obtained after subjecting inulin to two treatments with methyl sulphate and sodium hydroxide. A specimen of this material, freely soluble in boiling ether, gave C = 52·14, H = 7·63, OMe =39·0 per cent. 14·5 Grams were subjected to one methylation by the silver oxide reaction, the procedure being exactly as described by Irvine and Steele. Contrary to expectation, the product was no longer entirely soluble in boiling ether, and was thus divisible into two fractions, showing, however, the same composition after drying at 65°/150 mm.

(*a*) *Fraction soluble in ether* (yield 51 per cent.).
C = 53·11; H = 7·70; OMe = 44·4 per cent.
$[\alpha]_D^{20°}$ in chloroform solution = − 46·62° for c = 1·552.

(*b*) *Fraction insoluble in ether* (yield 28 per cent.).
C = 52·90; H = 7·78; OMe = 44·0 per cent.
$[\alpha]_D^{20°}$ in chloroform solution = − 49·25° for c = 1·711.

As trimethyl inulin requires C = 52·94; H = 7·84; OMe = 44·0 per cent., the agreement is satisfactory, and the rotations approximate to that of Karrer's specimen. At least three forms of trimethyl inulin have thus been isolated: (1) soluble in ether and dextrorotatory, (2) soluble in ether and lævorotatory, (3) insoluble in ether and lævorotatory. The description of a fourth variety will form the subject of a future communication. Meanwhile, of the three distinctive types mentioned above, (1) has already been shown to give trimethyl γ-fructose on hydrolysis, and similar tests were therefore applied to (2) and (3).

Conversion of the Soluble Lævorotatory Form of Trimethyl Inulin into Dextro-trimethyl γ-Fructose.

Oxalic acid was used as the hydrolytic agent and, for reasons already given, dilute solutions were employed. A 2 per cent. solution of the trimethyl inulin was prepared in 66 per cent. aqueous alcohol containing 0·4 per cent. of oxalic acid and, after filtration, was heated at 90°, polarimetric readings being taken every thirty minutes. Typical observations are given below, the specific rotations being calculated on the initial concentration.

Time from start.	$[\alpha]_D^{15°}$.	Time from start.	$[\alpha]_D^{15°}$.
30 minutes	− 38·8°	6 hours	+ 11·6°
1 hour	− 34·6	9 ,,	+ 22·8
3 hours	− 13·6	11 ,,	+ 26·6
4½ ,,	Inactive		

When the rotation became constant the sugar was separated and purified in the usual manner. In this way, trimethyl γ-fructose was obtained, identical in every respect with the sugar isolated in a similar reaction from dextrorotatory trimethyl inulin [Found: C = 48·74; H = 7·96; OMe = 40·76. $C_6H_9O_3(OMe)_3$ requires C = 48·75; H = 8·11; OMe = 41·88 per cent.]. $[\alpha]_D^{20°}$ in chloroform solution = + 24·8° for $c = 1$, the standard value being + 26·6°.

The proof was extended by converting 5 grams of the sugar into tetramethyl γ-fructose in the following reactions.

(*a*) *Conversion into Trimethyl γ-Methylfructoside.*—This reaction was carried out by preserving a 2 per cent. solution of the sugar in methyl alcohol containing 0·25 per cent. of hydrogen chloride for nine hours at 30°. The permanent rotation of the solution was $[\alpha]_D$ + 57·5° (Irvine and Steele, *loc. cit.*, quote + 57·0°) and the subsequent treatment was as usual.

(*b*) *Methylation of Trimethyl γ-Methylfructoside.*—Two methylations by means of the silver oxide reaction sufficed to give the fully methylated fructoside, which was isolated in the manner described in former papers.

(*c*) *Hydrolysis of Tetramethyl γ-Methylfructoside.*—Following the standard processes and using 0·25 per cent. hydrochloric acid as the hydrolytic agent, complete hydrolysis was effected at 90°. The permanent specific rotation attained by the solution was + 32·0°, which, considering the extreme sensitiveness of the activity of fructose derivatives towards changes in temperature, is in good agreement with the value found by Irvine and Steele ($[\alpha]_D$ + 30·7°). The tetramethyl fructose produced was isolated as a mobile syrup, which was purified by two distillations under the high vacuum of the Gaede pump (Found: C = 51·02; H = 8·46; OMe = 50·7. Calc., C = 50·85; H = 8·47; OMe = 52·5 per cent.). The sugar displayed all the characteristic properties of a γ-form, reducing potassium permanganate, Fehling's solution, and ammoniacal silver nitrate solution in the cold. Its identity with tetramethyl γ-fructose was further confirmed by the determination of the specific rotation.

Hydrolysis of the Form of Trimethyl Inulin Insoluble in Ether.

In general, the series of processes just described was applied to this particular variety of trimethyl inulin, minor variations being necessary on account of the different solubility.

A 2 per cent. solution of the compound in 66 per cent. alcohol containing 1 per cent. of oxalic acid was boiled under a reflux condenser. In this case also, as hydrolysis proceeded, the rotation altered from lævo to dextro and attained the same constant value. The trimethyl γ-fructose ultimately obtained showed a slightly lower

specific rotation in chloroform solution than the standard value ($[\alpha]_D + 24 \cdot 6°$ in place of $26 \cdot 6°$), but was otherwise identical with previous preparations. As a final confirmation of the γ-structure of the sugar, it was in turn converted into trimethyl methylfructoside, tetramethyl methylfructoside, and tetramethyl fructose. The final product was identical in composition and properties with the specimen of tetramethyl γ-fructose produced in the hydrolysis of the other varieties of trimethyl inulin.

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CXXX.—*Photocatalysis. Part II. The Photosynthesis of Nitrogen Compounds from Nitrates and Carbon Dioxide.*

By EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and DONALD PRYCE HUDSON.

THE mechanism of the photosynthesis of formaldehyde from carbon dioxide and water was dealt with in the previous paper (Baly, Heilbron, and Barker, T., 1921, **119**, 1025) and it was shown that the reaction is purely a photochemical one. Formaldehyde is synthesised in aqueous solutions of carbon dioxide under the influence of light of very short wave-length ($\lambda = 200\mu\mu$) and, further, the synthesis takes place under the influence of visible light in the presence of visibly coloured substances which have the power of forming labile additive compounds with the carbonic acid. It was further shown that formaldehyde, when exposed in aqueous solution to ultra-violet light of wave-length $290\mu\mu$, is readily polymerised to reducing sugars. By the action of the light, the formaldehyde molecule is converted into the active phase, which at once undergoes polymerisation to sugars. This active phase is the same as that which is the first product of the photosynthesis from carbonic acid and, therefore, in the living plant sugars are produced directly without the actual formation of the ordinary non-reactive molecules of formaldehyde.

These preliminary results suggested to us several lines along which further investigation should be made and each of these has afforded results of considerable interest which we hope shortly to

ι a position to publish. In the present paper we wish to discuss :ormation of the complex nitrogen derivatives in the living plant. ıere is little doubt that the original source of the nitrogen t be potassium nitrate or, possibly, ammonium salts, and the stion to be answered is whether the plant is able to synthesise ı one or both of these sources by the use of activated form-:hyde the many complex nitrogenous substances that have been ıd in the vegetable kingdom. Two separate investigations e been undertaken, one with potassium nitrate and the other h ammonia, and the results we have obtained in each case are y interesting. We propose in what follows to restrict ourselves inly to an account of our work with potassium nitrate.

:t was shown by Moore and Webster (*Proc. Roy. Soc.*, 1919, }, **90**, 158) that nitrates are rapidly reduced to nitrites by ultra-›let light, and the suggestion was made by them that this photo-emical change is the first step in the synthesis of the naturally :urring nitrogen compounds, but they did not indicate the ınner in which the nitrites are utilised in the plant. Although is photochemical observation has been confirmed by us, it would em to be of little importance as far as the vital synthesis is con-rned, since it is in the highest degree improbable that the ultra-olet light can penetrate the highly absorbing cellular tissues of ıe plant. Further, it has been proved that potassium nitrate is :duced to nitrite within the roots and stems of plants, where bviously no photochemical reaction is possible.

Now it has been shown by Schimper (*Bot. Z.*, 1888, **46**, 65) that itrites are always present in the living leaf when the plant is in he dark and that they disappear when the leaf is exposed to light. Moreover, the disappearance of the nitrites only takes place when :hlorophyll is present, since, when a partly etiolated leaf is illumin-ated, the nitrites remain unaltered in those portions of the leaf which contain no chlorophyll. We have found that activated formaldehyde readily combines with potassium nitrite to give formhydroxamic acid and also that this substance at once reacts with more molecules of activated formaldehyde to produce a great variety of complex substances such as are found in the living plant. This photosynthetic production of formhydroxamic acid was first discovered by Baudisch (*Ber.*, 1911, **44**, 1009), who exposed an aqueous solution of potassium nitrite, containing methyl alcohol, to ultra-violet light. We have proved that the reaction takes place between activated formaldehyde and the nitrite by passing carbon dioxide through aqueous solutions of either potassium nitrate or nitrite which were exposed to ultra-violet light, and also by exposing solutions of the nitrate or nitrite containing form-

aldehyde to the light. In each case the production of formhydroxamic acid was proved by means of its copper salt, whilst none was formed when a solution of potassium nitrite and formaldehyde was allowed to remain in the dark even at 100°. We have further found that no reducing sugars are formed when sufficient nitrite is present to react with all the activated formaldehyde, but that, if the activated formaldehyde is produced in excess of that utilised by the nitrite, reducing sugars are produced.

Three important conclusions may be drawn from these facts :

1. Activated formaldehyde such as is photosynthetically produced reacts with potassium nitrite.

2. This reaction takes precedence of the polymerisation of the activated formaldehyde to reducing sugars.

3. When the activated formaldehyde is produced at a rate greater than that at which it can react with the nitrite and with the formhydroxamic acid thus formed, the excess polymerises to reducing sugars. In this case, the two reactions take place simultaneously and independently.

The extraordinary readiness with which activated formaldehyde reacts with potassium nitrite or polymerises to form reducing sugars shows that it differs very materially from the substance in its ordinary form. The reaction whereby carbon monoxide is prepared by the dehydration of formic acid has not yet been reversed, that is to say, formic acid has not been obtained by the direct action of carbon monoxide on water. There is no doubt that this reaction would take place photochemically in the presence of light of very short wave-length, such as is required to activate the carbon monoxide molecule. The freshly-synthesised molecule of formic acid would then doubtless be formed in accordance with the scheme

$$C{=}O + H_2O = C{<}^{OH}_{OH} \longrightarrow H{-}C{\leqslant}^{O}_{OH},$$

that is to say, when freshly synthesised, the constitution of formic acid is to be represented as the true hydrate of carbon monoxide, a derivative of bivalent carbon. This configuration being metastable, the molecule loses energy and passes into the ordinary phase. By analogy, the freshly synthesised or photochemically activated molecule of formaldehyde would have the constitution H·C·OH, and this formula well explains the extraordinary reactivity of this substance. Its rapid polymerisation to sugars becomes obvious and its union with potassium nitrite to give formhydroxamic acid will take place as follows :

$$H{-}C{-}OH + O{=}N{-}OK = \begin{array}{c} H{-}C{-}OH \\ \| \\ O{=}N{-}OK \end{array} = \begin{array}{c} H{-}C{-}OH \\ \| \\ N{-}OK \end{array} + O,$$

the potassium salt being completely hydrolysed to the free acid.

There is no doubt that formhydroxamic acid marks the first step the phytosynthesis of the nitrogen compounds found in the ant. We have proved this, not only by the fact that this com-und is actually produced by the direct action of activated rmaldehyde on potassium nitrite, but also by the fact that form-droxamic acid reacts with activated formaldehyde to give mpounds which are known to occur in the living plant. An ueous solution of formhydroxamic acid is only very slowly acted n by ultra-violet light, and, further, no change occurs on keeping e solution of the acid and formaldehyde in the dark. If the tter solution is exposed to ultra-violet light, both the form-ydroxamic acid and the formaldehyde rapidly disappear, the test or sugars always being negative unless the aldehyde is present in xcess. We have further found that by the action of ultra-violet ight on an aqueous solution of potassium nitrite and formaldehyde, ubstances more complex than formhydroxamic acid are formed, lthough this is the first compound produced. Our results therefore xplain the observations made by Schimper which were referred o above.

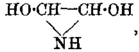
Since the formation of formhydroxamic acid is the first step in the synthesis, we have used in the greater number of our experiments a preparation of this compound obtained by the action of ethyl formate on hydroxylamine in methyl-alcoholic solution. Aqueous solutions of this acid were prepared, and these, after the addition of formaldehyde, were exposed to ultra-violet light. The products formed vary considerably with the relative concentrations of the acid and formaldehyde, and the difficulties are considerably increased by the very remarkable velocity of the reactions. Substances are produced in the first hour, only to give place shortly afterwards to more complex compounds by further condensation with activated formaldehyde.

The variation in the results that we have obtained establishes the fact that there are at least three ways in which activated formaldehyde can condense with formhydroxamic acid, a conclusion which may also be drawn from Baudisch's work. In discussing these condensations, reference must be made to our investigation of the polymerisation of activated formaldehyde to sugars. The results that we have obtained prove that only hexoses are formed, all tests for pentoses in the sugar syrup having proved to be negative. We hope to communicate the experimental proof of this and to discuss its importance in phytosynthesis in a further paper. The fact that hexoses only are formed shows that in all probability the polymerisation takes place to give the product which is most favoured by spatial configuration. It justifies us in assuming that

the same is true of the nitrogen synthesis and that in the condensation of formhydroxamic acid with activated formaldehyde the first products are those which are most favoured by spatial configuration.

Before dealing with this, we may record the fact that we have definitely proved the formation of α-amino-acids and, further, in some experiments we found that methylamine was formed. Whilst it is possible that methylamine is produced directly from formhydroxamic acid, we believe that it arises from the action of activated formaldehyde on ammonia. We frequently found small quantities of ammonia in our solutions after exposure to light, and further, we have proved that activated formaldehyde does react with ammonia to give methylamine. This is of some interest since it affords a direct experimental proof of Pictet's contention that in phytosynthesis formaldehyde acts as a methylating agent, it being remembered, however, that this is a reaction peculiar to the active formaldehyde that is photosynthetically produced.

We would mention here an observation which is of considerable importance with reference to the mechanism of the synthesis of compounds by the action of activated formaldehyde on formhydroxamic acid. In all these reactions oxygen is set free, a fact that is proved by the oxidation of considerable quantities of the formaldehyde to formic acid, a phenomenon which does not occur when aqueous solutions of formaldehyde are exposed to ultraviolet light. This leads to the view that formhydroxamic acid readily loses oxygen and indeed that at the moment of its reaction it may be represented as $\underset{\|}{\text{H—C—OH}}^{*}$ / NH. This molecule can react with activated formaldehyde in several ways. In the first place it can combine with one molecule of activated formaldehyde to give the labile ring compound

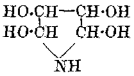


, which by rearrangement would doubtless give glycine. Then, again, since the amino-group is protected by internal salt formation, the median CH_2 group of glycine may react with more molecules of the activated formaldehyde to give the homologues of glycine. This scheme necessitates that every acid must have the amino-group in the α-position, which, of course, is invariably the case in phytosynthesis. We proved the formation of α-amino-acids in our experiments by the so-called ninhydrin reaction, which is specific for these sub-

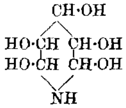
* It may be noted that this substance is a hydrate of hydrocyanic acid, a fact to which we would direct attention in connexion with the formation of cyanogenetic glucosides.

stances, a pure blue colour being developed on heating with an aqueous solution of triketohydrindene hydrate. We have succeeded in isolating these acids in the form of their hydrochlorides, but have not yet succeeded in identifying them. Baudisch states (*Z. angew. Chem.*, 1913, **26**, 612) that he obtained evidence of the formation of substances of the nature of α-amino-acids.

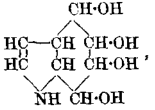
A second direction along which the synthesis may proceed is by the union of several molecules of activated formaldehyde with one molecule of formhydroxamic acid. If we argue from the spatial configuration, the two most stable configurations would be the ring compounds formed by the condensation of either three or four molecules of the formaldehyde with one molecule of formhydroxamic acid, namely,



and



These compounds, by the loss of oxygen and of water, would give pyrrolidine or pyrrole compounds and piperidine or pyridine compounds, respectively. Then again pyrrole and pyridine may condense with more molecules of the activated formaldehyde to give indole compounds on the one hand and quinoline and *iso*quinoline on the other. For example, in the case of pyrrole the first product of the condensation would be



which by loss of oxygen and water would give indole.

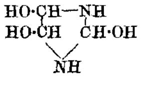
The simplicity of these syntheses is peculiarly attractive, for they are the natural result of bringing together potassium nitrite and the activated formaldehyde which is photosynthetically produced from carbonic acid by the photocatalytic agency of the chlorophyll. They are, moreover, not too speculative, since Baudisch states that he has proved the presence of both pyrrole and pyridine derivatives in solutions of potassium nitrite and methyl alcohol after long exposure to sunlight. In our experiments with formhydroxamic acid, using the artificial light of the quartz-mercury lamp, we have not as yet found evidence of the formation of any simple derivatives of either pyrrole or pyridine, but, as

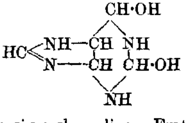
already explained, the photosynthesis under these conditions is extraordinarily rapid and very soon goes far beyond the formation of simple compounds. If a solution of formhydroxamic acid containing formaldehyde is exposed for twelve hours to the light of the quartz-mercury lamp, evaporated to dryness with hydrochloric acid, and the residue made alkaline with sodium hydroxide, and extracted with ether, the ethereal extract on evaporation always gives a nitrogen base which is of an alkaloidal nature. We have obtained at least two different alkaloids in this way, one of which is a volatile oil with an odour resembling that of tobacco, whilst the other is a solid of low melting point with an odour resembling that of burnt feathers. Both these substances form crystalline salts with acids and give strong positive tests with all the usual reagents for alkaloids. We have not as yet been able to prepare sufficient of these compounds for their identification. It may be noted that the first-mentioned alkaloid is probably identical with that obtained by Baudisch (*Ber.*, 1913, **46**, 115).

Strong confirmatory evidence of the reality of the above syntheses is also to be found in the fact that pyridine is formed by the action of activated formaldehyde on ammonia. Although the pyridine is produced by the condensation of five molecules of the formaldehyde with one molecule of ammonia instead of four molecules with one of formhydroxamic acid, this observation clearly establishes the fact that the synthesis takes place along the lines indicated above.*

We have also carried out some experiments on the action of activated formaldehyde on pyridine, and although these are still incomplete the results that we have obtained support the views we advance as to the mechanism of the synthesis.

There yet remains to be considered another direction along which the condensation of formhydroxamic acid with activated formaldehyde can proceed. Two molecules of formhydroxamic acid can condense with one molecule of the formaldehyde to give I,

(I.) 

 (II.)

which by loss of oxygen and water gives glyoxaline. Furthermore, it is possible that a molecule of glyoxaline will condense with two

* This observation has been made by Mr. H. J. Stern, with whom we are investigating the action of activated formaldehyde on ammonia. We hope shortly to publish the results of this work.

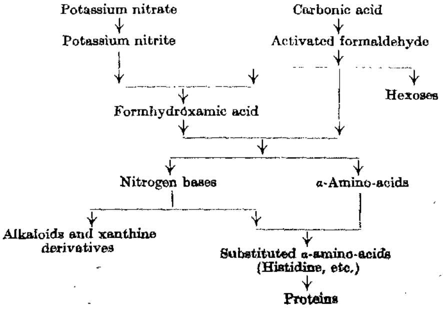
more molecules of formhydroxamic acid to give II, which is a xanthine derivative, and it may be suggested that the phytosynthetic production of xanthine, theobromine, and caffeine follows this course. Here, again, we are able to bring forward evidence in support. In one experiment in which a solution of formhydroxamic acid containing only a small quantity of formaldehyde had been illuminated for two hours a small quantity of a crystalline nitrogen base was obtained. This compound melted between 85° and 90°, was odourless when cold and developed a fish-like smell on warming, gave a white silver salt, and was readily oxidised to formic acid by cold, neutral potassium permanganate. We believe that in this case glyoxaline was produced. We have also obtained evidence of the formation of glyoxaline in other experiments, but in these cases the product was a mixture. The odour of glyoxaline was very noticeable on warming, the reactions with silver nitrate and potassium permanganate were equally definite, but we were unable to isolate the glyoxaline in the crystalline form. The formation of glyoxaline would remove our suggested explanation of the phytosynthesis of xanthine derivatives from the realms of speculation, and the experimental results we have obtained lead us to place considerable confidence in its truth.

We stated above that we had obtained positive evidence of the photosynthetic production of α-amino-acids from potassium nitrite and formaldehyde, and we are also able to state that we have succeeded in proving the formation of at least one substituted α-amino-acid. The alkaline solution after the extraction of the alkaloids by means of ether is acidified with hydrochloric acid and evaporated to dryness on the water-bath and the solid residue is extracted with boiling alcohol (90 per cent.). To the alcoholic extract is added a mixture of absolute alcohol and ether to precipitate the inorganic salts, and the filtrate is evaporated to dryness. The residue consists of the hydrochlorides of at least one substituted α-amino-acid and gives after neutralisation with sodium carbonate the very characteristic Burgundy-red colour on heating with triketohydrindene hydrate. These acids do not give the usual blue copper salt characteristic of the ordinary simple α-amino-acid. Whilst we have not been able to identify these acids, the colour reaction with diazobenzenesulphonic acid leads us to believe that histidine is present. The formation of histidine would, of course, materially strengthen the arguments for the formation of glyoxaline and the xanthine synthesis suggested above.

The formation of a substituted α-amino-acid is undoubtedly a matter of great interest, but we would point out that it is a natural consequence of the photosynthetic process. The fact that acids

of the type of histidine, tryptophan, etc., are readily formed is proved by their occurrence in the living plant. Our results establish the fact that the syntheses of nitrogen bases and of α-amino-acids take place concurrently when formaldehyde is photosynthetically produced in the presence of potassium nitrite. Since both types of compound, when first synthesised, exist in a highly reactive phase, their combination to form substituted α-amino-acids ensues withont difficulty. The phytosynthesis of proteins is only one stage further in the process, namely, the intercondensation of the various substituted α-amino-acids, again a natural consequence of their existing in highly reactive phases when first synthesised. Although we have not yet found any evidence of protein formation, our results seem to indicate the manner in which these bodies are synthesised in the living plant.

Once more we would emphasise the essential difference between the conditions in the living plant and those in the laboratory, namely, the control that is present in the one and completely absent in the other. This want of control very materially increases the difficulty of experiments *in vitro*, owing to the number of products that are formed in small quantities. Although we have succeeded in establishing the various types of compounds that are formed, the identification of the individual substances is extremely troublesome. In spite of the many difficulties, we feel that our results not only clearly establish the initial stages of the phytosynthesis of nitrogen compounds, but also indicate the main lines along which this phytosynthesis takes place. The following table shows the general scheme which our results lead us to put forward with some confidence.



The activated formaldehyde produced by the photocatalytic action of chlorophyll on carbonic acid combines with the potassium nitrite known to be present in the leaves, this reaction taking precedence of all others. The formhydroxamic acid then condenses with more activated formaldehyde, this reaction taking second place in the order of precedence, whilst all excess of the activated formaldehyde polymerises to form hexoses.

The interaction of the activated formaldehyde with formhydroxamic acid follows two main lines, the formation of α-amino-acids and of various nitrogen bases. These nitrogen bases consist of various types, namely, pyrrole, pyridine, and glyoxaline, which by further condensation with activated formaldehyde give indole, quinoline, *iso*quinoline, and xanthine derivatives. In cases where such is possible these bases condense with the α-amino-acids to give the substituted α-amino-acids such as histidine, tryptophan, etc. The excess of nitrogen bases undergoes further condensation to give alkaloids, whilst the substituted α-amino-acids interact to give proteins. The readiness with which all these reactions take place is due to the cardinal fact that the various compounds are produced in highly reactive phases, analogous to the highly reactive phase of formaldehyde when photosynthetically formed. This reactivity enables condensations to occur which are otherwise impossible to realise in the laboratory. It is a matter of common knowledge that these reactions must occur in the living plant, and our results show that the key to the problem is the enhanced reactivity of freshly synthesised molecules.

In communicating this report on our work we would direct attention to some general conclusions of great importance. Our results leave no doubt that the activated formaldehyde photosynthetically produced in the living chloroplast reacts with potassium nitrite with extraordinary ease to produce formhydroxamic acid, which at once proceeds to condense with more of the activated formaldehyde to give various nitrogen compounds. It follows from this that the synthesis of the nitrogen compounds found in the plant is not photosynthetic except in so far as the production of the activated formaldehyde by the chlorophyll is concerned. The various amino-acids, proteins, alkaloids, etc., are natural and indeed inevitable results of the photosynthesis of formaldehyde in the presence of potassium nitrite. Their formation has been considered by some to savour of the mysterious, the mystery being found in the question as to how a plant succeeds in synthesising the very substances it requires for its existence. The life and growth of a plant consist in the utilisation of the products formed in its leaves. There is no real mystery in the formation of

these products, the plant has no choice in the matter, since with the given conditions of chlorophyll, carbonic acid, light energy, and potassium nitrite the synthesis must follow its natural course just as we have found to take place *in vitro*.

A further conclusion of importance is that the region where the synthesis occurs must necessarily be restricted to the leaves. Since it must not be forgotten that the synthesis of hexoses is taking place concurrently, the conditions are perfect for the formation of glucosides and we believe that the products of the nitrogen synthesis are translocated as soluble glucosides. The fact that nitrogen derivatives are found in other parts of the plant cannot be accepted as an argument that they must have been synthesised in those parts. There can be no doubt that the synthesis takes place in the leaves and that the compounds are subsequently distributed as soluble glucosides by the normal translocatory processes.

Finally, we would direct attention to the fact that in the various stages of the nitrogen synthesis oxygen is evolved. It is interesting to note the presence of the enzyme catalase in the leaves which has the power of accelerating the loss of oxygen by various compounds. Very possibly too it is this enzyme that causes the reduction of potassium nitrate to nitrite. The escape of oxygen in the various stages of the nitrogen synthesis is therefore certainly not antagonistic to the conditions known to exist in the plant. As already stated, the evolution of oxygen in our experiments was proved by the oxidation of considerable quantities of formaldehyde to formic acid.

In conclusion, we tender our thanks to the Department of Scientific and Industrial Research for a grant to one of us (D. P. H.) which has enabled this investigation to be carried out.

THE UNIVERSITY,
LIVERPOOL. [*Received, April 22nd*, 1922.]

CXXXI.—*The Potassium Salt of Hexahydrodioxydiboron.*

By RAMES CHANDRA RAY.

It has been shown in conjunction with Travers and Gupta (Pamphlet, H. K. Lewis and Co., 1916) that when magnesium boride, prepared by heating an intimate mixture of 1 part of boron trioxide with nearly 2¼ parts of magnesium powder at a red heat, is treated with water, hydrogen is evolved—rapidly at first and afterwards

e slowly—but practically no magnesium borate or boric acid 'oduced. The hydrogen evolved contains only traces of boron rides, which impart to it a characteristic odour. The solutions ained show the remarkable property of evolving hydrogen with k effervescence on addition of acid, and the acidified solution orbs iodine. They are very unstable and decompose at the nary temperature with evolution of hydrogen. Generally aking, the borohydrate solutions behave towards organic and rganic compounds as powerful reducing agents. They pre-tate the heavy metals from solutions of their salts. With pper sulphate, a red precipitate of copper hydride, which is ible in potassium cyanide, or a black precipitate containing pper and boron, is thrown down, according to the strength of solutions. From an extensive study of these solutions, it was ncluded that the solutions contained the compound which might represented by the empirical formula $H_6B_2O_2$ with a certain nount of magnesia. On keeping these solutions in a sealed tube, rticularly after addition of ammonia to them, a change took ace involving an increase in the quantity of hydrogen which uld be eliminated by the addition of acid. It was therefore ggested that the solutions contained two compounds partly presented by the formulæ $H_4H_2B_2O_2$ and $H_2H_4B_2O_2$, where H as the hydrogen given off on the addition of acid. The ratio of e hydrogen evolved on the addition of acid to the iodine which as absorbed by the acid solution also supported this view. It ay be added that the elimination of three atoms of hydrogen at time from a compound of the formula $H_6B_2O_2$ would be very ifficult to explain. It was found that the residue obtained on vaporating the solutions always contained magnesia and water n combination, and that the value of the ratio $B/(MgO + H_2O)$ vas very nearly 2, which suggests that one of the two compounds has the formula $H_6B_2O_2,H_2O$.

Neither of these compounds nor their magnesium salts could, however, be isolated from the solutions. It was considered that the potassium salt would probably be more stable, and the present investigation was undertaken with a view to isolate the potassium salt of one or both the isomerides.

The magnesium boride was prepared in the manner described in the pamphlet already referred to, and only those samples were used in which the reaction between boron trioxide and magnesium powder was complete, which was indicated by a gentle deflagration which took place when the mixture was being heated. The solution obtained by the action of water on magnesium boride was treated with $N/20$-potassium hydroxide until no further precipitation of

magnesium hydroxide took place. It was quickly filtered and the solution evaporated in a vacuum at the ordinary temperature and fractionally crystallised. The first fraction contained, chiefly, potassium metaborate and magnesium hydroxide. The liquid was drained off through a very small filter plate, and from this a crystalline deposit was finally obtained when nearly the whole of the water had evaporated, indicating that the substance was highly soluble in water. A large excess of potassium hydroxide was avoided, otherwise on evaporation a viscous, syrupy residue was obtained, from which it was extremely difficult to separate the crystalline substance. The crystals obtained in this way from a large number of fresh solutions were collected, the quantity obtained from each solution being very small. When a fairly large amount of the substance had been obtained, it was washed with methyl alcohol, in which it is not very soluble, in order to remove potassium hydroxide. It was recrystallised two or three times in a vacuum from water free from carbon dioxide, which appeared to bring about partial decomposition of the substance.

It was found that the same substance could be obtained somewhat more easily if the magnesium boride was directly treated with dilute potassium hydroxide solution. The solution obtained in this way behaves very similarly to that obtained by the action of water and contains only traces of magnesium. In this case also the concentration of the substance in the solution, although greater than that in the aqueous solution, is limited. This supports the view that the soluble solid compounds of boron, hydrogen, and oxygen are formed as a result of secondary reactions; an equilibrium appears to be established, after which further concentration of the substance does not take place. The solution obtained by the action of dilute potassium hydroxide on magnesium boride did not contain much free alkali and was treated in the same manner as described above. The difficulty of the preparation will be evident from the fact that not more than 2 to 3 grams of the crude substance could be obtained from each extract, and altogether only 10 to 12 grams of the pure substance were obtained.

The pure substance is colourless and possesses a well-defined crystalline form, probably belonging to the cubic system. It is slightly deliquescent and easily soluble in water. It is quite stable when preserved free from carbon dioxide and moisture. An aqueous solution of the substance shows an alkaline reaction, evolves hydrogen slowly when left exposed to air, acts as a powerful reducing agent, and behaves similarly to the borohydrate solution (*loc. cit.*). The salt is decomposed by acids with evolution of large quantities of hydrogen. Strong nitric acid acts on the

tance vigorously and so much heat is generated that the ogen evolved catches fire.

weighed *quantity* of the substance was dissolved in 10 c.c. of lled water (free from carbon dioxide) in a distilling flask, :h was then connected with a mercury pump and evacuated. ıte sulphuric acid (25 c.c.) was run into the flask and the hydrogen lved was collected and measured. The liquid in the flask was hed out into a stoppered bottle and kept in the dark for three rs with 25 c.c. of $N/10$-iodine solution. The iodine absorbed the acidified solution was determined against a blank experiment ried out in a similar stoppered bottle containing 10 c.c. of dis-ed water, 25 c.c. of dilute sulphuric acid, and the same quantity iodine solution. The following results were obtained :—

Vt. of salt in gram.	C.c. of hydrogen (reduced to *N.T.P.*) evolved on the addition of acid.	C.c. of $N/10$-iodine absorbed by the acidified solution.	Gram-equivalent of hydrogen.	Gram-equivalent of iodine.	Ratio I/H.
)·1236	41·2	18·0	0·00371	0·00180	0·49
0·0985	32·0	14·8	0·00288	0·00148	0·51
0·1568	50·9	23·0	0·00458	0·00230	0·50

he amounts of hydrogen given off by the action of acid in the ıree experiments are 3·00, 2·92, and 2·92 per cent. of the salt. 'he significance of the ratio I/H has been discussed fully in the amphlet above referred to.

The potassium content of the substance was estimated by dis-olving a weighed quantity of the substance in water and oxidising t by boiling with strong nitric acid in a platinum dish. The boric ıcid formed was removed by repeatedly evaporating with a mixture of methyl alcohol and hydrochloric acid. The potassium chloride was finally converted to sulphate and weighed as such. For the estimation of the boron content the following method was adopted. A weighed quantity of the substance was dissolved in a small quantity of water and sealed in a small bulb with 5 c.c. of strong nitric acid. The bulb was heated on a water-bath for three to four hours, after which the contents were washed out and evaporated to dryness in a vacuum desiccator. The boric acid in the residue was estimated by the Gooch-Rosenbladt method (*Z. anal. Chem.*, 1887, **26**, 21) by distilling with methyl alcohol. The trimethyl borate was condensed in a long, spiral condenser, through the outer jacket of which water, cooled by passing through a copper spiral packed in ice, was circulated. The methyl borate was hydrolysed with a known excess of pure lime, carefully evaporated,

and ignited. The increase of weight of the lime gave the weight of boron trioxide. The method gave excellent results and with a little care an accuracy of 0·05 per cent. could be easily obtained (Found: K = 56·96, 57·16, 57·42; B = 16·05, 15·95, 16·10; H = 3·00, 2·92, 2·92. $KO\cdot BH_2$ requires K = 57·35; B = 16·18; H = 2·94 per cent.).

The analytical results agree closely with the theoretical value for $KO\cdot B{:}H_2$ and it was expected that this would also represent the molecular composition of the substance, for in this case boron exhibits its normal valency. The measurement of the equivalent conductivity of solutions of the substance shows, however, that the substance possesses the molecular formula $K_2O_2B_2H_4$, and not $KOBH_2$. The conductivity measurements at 25° gave the following results:—

v	32	64	128	256	512	1024
μ	124·4	133·2	138·8	142·9	146·8	148·5
μ_v/μ_{1024}	0·84	0·90	0·93	0·96	0·99	—

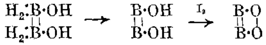
The difference in the equivalent conductivities of N/1024- and N/32-solutions is 24·1, which agrees well with the values obtained for dibasic alkali salts by Ostwald (*Z. physikal. Chem.*, 1887, **1**, 74), Walden (*ibid.*, 1887, **1**, 529; 1888, **2**, 49), and Bredig (*ibid.*, 1893, **12**, 230).

The isolation of the compound $K_2O_2B_2H_4$ confirms the presence of the compound $H_6B_2O_2$ in the borohydrate solution, obtained by the action of water on magnesium boride, which gave off four atoms of hydrogen by the action of acids, the other two atoms of hydrogen being removable by iodine. Although the presence of two isomeric compounds in the borohydrate solution was indicated by the study of these solutions, only one of the isomerides could be isolated by the action of potassium hydroxide. It is probable that this represents the more stable form. A similar change was caused in the borohydrate solutions by the action of ammonia and by increase of temperature. It should be mentioned in this connexion that in the aqueous solutions studied by Travers, Ray, and Gupta (*loc. cit.*) the compound $H_4H_2B_2O_2$ could never be obtained free from $H_2H_4B_2O_2$, although in the case of solutions obtained under certain conditions only the second compound appeared to be present.

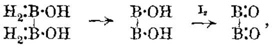
The action of acids on solutions of the salt $H_4B_2(OK)_2$ and of iodine on the acidified solutions may be represented by the equations (1) $H_4B_2(OK)_2 + 2H_2SO_4 = 2KHSO_4 + B_2(OH)_2 + 2H_2$ and (2) $B_2(OH)_2 + I_2 = B_2O_2 + 2HI$, respectively. It has been shown by Travers, Ray, and Gupta (*loc. cit.*) that although the oxide

O_2 is oxidised when boiled in air, it is not converted into boric id by the action of iodine. Since the compound is comparatively ıble and under the action of acids loses four atoms of hydrogen d is probably converted into the compound $H_2B_2O_2$, which in ; turn is changed into the oxide B_2O_2 by the action of iodine, it ›pears to be likely that it possesses a symmetrical constitution, ıving the four hydrogen atoms in adjacent positions. Then the ›nstitution of the compound $H_4B_2(OH)_2$ may be graphically ritten as I or II, and its reactions in acid solution and subsequently ith iodine may be represented as follows :

(*a*)

(I.) 

ır (*b*)

(II.) 

according as it is assumed that boron is quinquevalent or quadrivalent. The reactions (*a*) appear to be more probable because of the peculiar properties of the oxide B_2O_2, which is not oxidised by iodine or certain other reagents, and also because of their similarity to those of nitrogen compounds. It may also be pointed out that the group ⁝B⁝B⁝ is probably a stable one, being also present in the compounds of boron and hydrogen described by Stock and Frederici (*Ber.*, 1913, **46**, 1959), to which the formulæ $H_3B{:}BH_3$ and $H_3B{:}BH_2{\cdot}BH_2{:}BH_3$ may be assigned. It may be possible to isolate the compound $H_2B_2O_2$ and the oxide B_2O_2 from the potassium salt $H_4B_2(OK)_2$, and it is intended to make this the subject of a later communication.

Stock and Kuss (*Ber.*, 1914, **47**, 810) have shown that a similar compound, to which they ascribe the formula $KOBH_3$, is formed by the action of either of the hydrides B_2H_6 or B_4H_{10} on potassium hydroxide. They isolated this substance by dissolving potassium hydroxide in one and a half times its volume of water and treating it with B_4H_{10} at 0°. The properties of this substance are in many respects similar to those of the potassium salt described in this paper. Stock and Kuss (*loc. cit.*) have not studied the action of acid on $KOBH_3$, neither have they determined its molecular weight. It is possible that both the substances are formed in the same way; a more hydrogenated compound is first formed, and this loses hydrogen and is converted into the second substance.

The action of chlorine and bromine on the hydride B_2H_6 has been studied by Stock, Kuss, and Priess (*Ber.*, 1914, **47**, 3115), who have described the formation of a product having the com·

position $B_2H_4X_2$, where X represents a halogen element. Hexahydrodioxydiboron, the potassium salt of which is described in this paper, may be regarded as a similar compound in which the two halogen atoms have been replaced by two hydroxyl groups. Stock and his co-workers have suggested that boron is quadrivalent in the case of its hydrides and certain compounds derived from it, but except in cases in which the composition of the substance is douhtful or the molecular formula has not been determined, it is possible to assign formulæ to all these compounds on the assumption that boron is always tervalent or quinquevalent. The quinquevalent nature of boron is supported by the existence of boron pentasulphide, prepared by Moissan (*Compt. rend.*, 1892, **115**, 271), and a few other compounds containing organic radicles such as $C_6H_5{\cdot}BCl_4$, $(CH_3)_3{\cdot}B{:}NH_3$, $(C_2H_5{\cdot}O)_3B(C_2H_5){\cdot}ONa$, etc. The existence of certain additive compounds of boron trihaloids also suggests that boron is pentad in some of its compounds.

Summary.

(1) *The presence of hexahydrodioxydiboron,* $H_4B_2(OH)_2$, *in the* solution obtained by the action of water on magnesium boride is confirmed.

(2) The potassium salt, $H_4B_2(OK)_2$, has been isolated from the solution. This substance is also formed when magnesium boride is directly treated with dilute potassium hydroxide solution. The formula of the compound has been established from analytical results and conductivity determinations.

(3) The properties of this salt have been described. It is fairly stable in absence of moisture and carbon dioxide, and generally behaves as a powerful reducing agent.

(4) The solution of the salt, which is highly soluble in water, behaves similarly to the borohydrate solution.

(5) The salt loses four atoms of hydrogen when treated with an acid, and the acidified solution absorbs two atoms of iodine per molecule of the salt.

In conclusion, I should like to offer my best thanks to Dr. M. W. Travers, F.R.S., for the valuable suggestions and help I have received from him. My thanks are also due to Prof. F. G. Donnan, F.R.S., for his kind criticism and interest.

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CXXXII.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part III. Unsymmetrical Hydroxy- and Methoxy-derivatives.*

By Johannes Sybrandt Buck and Isidor Morris Heilbron.

It has previously been shown (Heilbron and Buck, T., 1921, **119**, 1500) that *p*-dimethylaminobenzaldehyde readily condenses with *o*-hydroxystyryl methyl ketone, in presence of alkali, to yield a complex composed of one molecule of 4′-dimethylamino-2-hydroxydistyryl ketone and one molecule of *p*-dimethylaminobenzaldehyde, which latter component can be replaced by other compounds, such as benzene, alcohol, etc. The abnormal behaviour of this substance induced us to study in closer detail the methods of preparation, and the properties of other doubly-conjugated unsaturated ketones. On examining the literature it was found that, although various symmetrically substituted distyryl ketones had been prepared, the only unsymmetrical compound of this class, containing a 2-hydroxyl group, described, was 2-hydroxydistyryl ketone (Kostanecki and Maron, *Ber.*, 1898, **31**, 728). The authors have now condensed *o*-hydroxystyryl methyl ketone (Harries, *Ber.*, 1891, **24**, 3180) with various substituted benzaldehydes, in the presence of sodium hydroxide. In general, the reaction proceeds rapidly in the presence of strong alkali, so that by stopping the condensation after a determined period, a good yield of the unsymmetrically substituted ketone is obtained. If other conditions are applied, such as more dilute solutions or a longer reaction period, the yield is much diminished, and the product is contaminated with the corresponding symmetrically substituted ketones, which, as already shown (Heilbron and Buck, *loc. cit.*), tend to be produced by the fission of the first-formed unsymmetrical ketone.

In this work, very definite limitations soon became apparent. In no case could a substituted benzaldehyde, containing a *p*-hydroxyl group, be condensed by the above-described reaction, the unchanged reagents being recovered, or, on more vigorous treatment, oily or resinous substances being produced. Protocatechualdehyde, vanillin, β-resorcylaldehyde, and *p*-hydroxybenzaldehyde were investigated, but in no case could the desired condensation product be obtained, even under the most varied conditions. A similar difficulty was encountered by Perkin, Robinson, and Turner (T., 1908, **93**, 1085), who failed to condense β-resorcylaldehyde with 1-hydrindones, whereas *p*-methoxysalicylaldehyde readily entered into condensation (Perkin and Robinson, T., 1907, **91**, 1073). That,

however, the inhibiting factor is not due solely to the presence of a hydroxyl group in the para-position to the aldehydic group is shown by the fact that both *p*-hydroxybenzaldehyde and vanillin readily condense with acetone to yield the corresponding substituted styryl methyl ketones. On the other hand, we have failed to bring about condensation in alkaline solution between either protocatechualdehyde or β-resorcylaldehyde and acetone, and the conclusion may thus be drawn that an accumulation of hydroxyl groups in the aldehyde either inhibits the condensation altogether, or that condensation takes place, yielding the poly-hydroxy-unsaturated ketone, which, when formed, immediately breaks down under the conditions of the experiment.

In order to test the validity of the latter deduction, a condensation was attempted between *o*-hydroxystyryl methyl ketone and gentisaldehyde, in which no *p*-hydroxyl group is present. The result was somewhat unexpected, for although no unsymmetrical distyryl ketone was isolated as such, *o*-hydroxystyryl methyl ketone was recovered in a form hitherto unobserved, being obtained in colourless prisms, which melt at the same temperature as the ordinary yellow form, but exhibit very marked differences in behaviour.

The difference between the two forms does not appear explicable simply on the assumption of *cis*- and *trans*-isomerism, such as has been observed by Haber with piperonylideneacetone (*Ber.*, 1891, **24**, 618), but is probably dependent on the presence of an *o*-hydroxyl group forming, in one case, a ring system with the carbonyl oxygen atom, in the manner postulated in Part I of these communications. The whole question is at present being investigated in detail and will be dealt with in a separate paper.

The isolation of this new modification of *o*-hydroxystyryl methyl ketone appears to us only explicable on the assumption that condensation with formation of the unsymmetrical polyhydroxy-distyryl ketone must actually have taken place in the first instance, followed immediately by the fission of the labile condensation product. On this view, gentisaldehyde would function, until completely resinified by the alkali present, after the manner of an ordinary catalyst.

The failure to isolate polyhydroxy-unsymmetrical distyryl ketones cannot then be attributable to any peculiar property of the hydroxy-aldehydes themselves, but solely to the instability of such ketones in presence of alkali, this being most marked in those containing either a *p*-hydroxyl group in one of the benzene rings or an accumulation of such groups.

Control condensations were carried out where possible by the

converse method of condensing salicylaldehyde with a substituted styryl methyl ketone, but it was generally found that this reaction was unsatisfactory and the products obtained were oily in character and difficult to manipulate. 3-Methoxy-4-hydroxystyryl methyl ketone (vanillylideneacetone) and *p*-hydroxystyryl methyl ketone failed to condense with salicylaldehyde and were recovered unchanged from the reaction mixture.

The ketones described in the experimental part have not yet been fully examined as regards their activity, but this is less than in the case of 4′-dimethylamino-2-hydroxydistyryl ketone. None of the compounds combines with solvents, but the degree of additivity may be gauged by that of 4′-methoxy-2-hydroxydistyryl ketone, which forms additive compounds with *m*-dinitrobenzene and *p*-dimethylaminobenzaldehyde. The action of hydroxylamine, phenylhydrazine, and semicarbazide on these ketones also appears to be abnormal.

EXPERIMENTAL.

3′ : 2-*Dihydroxydistyryl Ketone*,

$$OH\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OH.$$

—Twelve grams of *m*-hydroxybenzaldehyde were dissolved, together with 16 grams of *o*-hydroxystyryl methyl ketone, in 70 c.c. of absolute alcohol, and the solution was treated with 24 c.c. of 50 per cent. sodium hydroxide solution (3 mols. NaOH). After standing for three hours at room temperature, the solution was diluted with water, cooled with ice, and carefully neutralised with dilute acetic acid. A semi-solid mass was thus precipitated, which was allowed to harden and twice crystallised from aqueous alcohol. The ketone obtained in this way was finally purified by boiling with benzene, in which it is very sparingly soluble, but which removes traces of some readily soluble impurity. It crystallises out with one molecule of water in the form of a yellowish-green, crystalline powder, melting at 137° with the production of a deep green liquid (Found: C = 71·6; H = 5·8. $C_{17}H_{14}O_3,H_2O$ requires C = 71·8; H = 5·6 per cent.).

In order to prove that the molecule of water is not constitutional, the *dibenzoyl* derivative was prepared. It forms pale yellow prisms melting at 112—113°, and corresponds with a simple dibenzoyl compound (Found: C = 78·24; H = 4·86. $C_{31}H_{22}O_5$ requires C = 78·48; H = 4·64 per cent.).

2′-*Methoxy-2-hydroxydistyryl Ketone*.—6·8 Grams of *o*-methoxybenzaldehyde and 8·1 grams of *o*-hydroxystyryl methyl ketone, dissolved in 25 c.c. of ethyl alcohol, were treated with 40 c.c. of 10 per cent. sodium hydroxide solution (2 mols. NaOH). After

leaving the mixture to stand, the sodium salt, which had separated out over-night in the form of dull red crystals, was filtered off, suspended in water, and decomposed with dilute acetic acid. The crude yellow precipitate thus obtained (13 grams) was purified by two recrystallisations from benzene, using animal charcoal as decolorising agent. When pure, the ketone forms a pale apple-green, crystalline mass, melting at 129°, moderately soluble in the usual solvents (Found: C = 76·9; H = 5·8. $C_{18}H_{16}O_3$ requires C = 77·0; H = 5·7 per cent.).

3′-Methoxy-2-hydroxydistyryl Ketone.—This ketone was only prepared with difficulty, very small yields being obtained. The following preparation was the best of several carried out. 6·8 Grams of *m*-methoxybenzaldehyde and 8·1 grams of *o*-hydroxystyryl methyl ketone were dissolved together in 25 c.c. of 92 per cent. alcohol, and the solution was then treated with 40 c.c. of 10 per cent. sodium hydroxide solution (2 mols.). After standing over-night, the mixture was diluted with water, cooled with ice, and neutralised with dilute acetic acid. The ketone was precipitated in yellow flocks which, on filtering, tended to yield a gum-like mass, which became superficially brown on standing in air. By working up the product from a benzene–ether mixture, with the addition of light petroleum, a yield of nodular yellow crystals (about 1·5 grams) was obtained. The remainder of the product formed a limpid yellow oil of unknown constitution. For analysis, the ketone was recrystallised from benzene, in which it is moderately soluble. It forms small, canary-yellow, crystalline nodules, and melts at 128° to a deep green liquid (Found: C = 77·1; H = 5·8. $C_{18}H_{16}O_3$ requires C = 77·0; H = 5·7 per cent.).

4′-Methoxy-2-hydroxydistyryl Ketone.—Twelve grams of o-hydroxystyryl methyl ketone and 13·6 grams of anisaldehyde were dissolved in 70 c.c. of absolute alcohol, and the solution was treated with 16 c.c. of 50 per cent. sodium hydroxide solution (2 mols. NaOH). On standing at room temperature, bright red needles of the sodium salt separated out. These were suspended in ice-water and decomposed with dilute acetic acid. A yellow, gummy product separated which, after hardening, was filtered off and recrystallised from aqueous acetone. For analysis, it was recrystallised twice from chloroform and finally from benzene. The ketone forms tiny, yellow needles, melting at 139° to a green liquid. It is moderately soluble in benzene or chloroform, and very soluble in alcohol or acetone (Found: C = 76·9; H = 5·7. $C_{18}H_{16}O_3$ requires C = 77·0; H = 5·7 per cent.).

The p-*dimethylaminobenzaldehyde* additive product is readily obtained by dissolving equimolecular portions of the aldehyde and

ketone in the minimum quantity of hot absolute alcohol, and allowing the mixture to cool. The compound separates out as lemon-yellow prisms, melting at 91—92° (Found: C = 75·3; H = 6·5. $C_{27}H_{27}O_4N$ requires C = 75·5; H = 6·3 per cent.).

The m-*dinitrobenzene* additive product, prepared in a similar manner, is obtained as an orange-coloured, crystalline powder, melting at 117° (Found: N = 6·2. $C_{24}H_{20}O_7N_2$ requires N = 6·2 per cent.).

3′ : 4′-*Dimethoxy-2-hydroxydistyryl Ketone*,

$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3(OMe)_2$.

—16·4 Grams of veratraldehyde and 16·2 grams of *o*-hydroxystyryl methyl ketone were dissolved together in 40 c.c. of absolute alcohol and treated with 16 c.c. of 50 per cent. sodium hydroxide solution (2 mols. NaOH). After the mixture had stood for ten minutes, 150 c.c. of water were added. The whole soon set to a solid mass, which was now again diluted with a further 100 c.c. of water. After three hours, the brilliant red needles of the sodium salt were filtered off, suspended in water, and decomposed with acetic acid. A yellow, gummy mass, which hardened on standing, was thus obtained, from which, however, the ketone was extremely difficult to obtain pure. Better results were obtained by first recrystallising the sodium salt from an alcohol–ethyl acetate mixture, then *suspending it in benzene, and decomposing it with the exact amount* of glacial acetic acid. On heating the mixture, the ketone went into solution and, after filtration, was allowed to crystallise out. This product was then repeatedly recrystallised from benzene, in which it is only moderately soluble, animal charcoal being used as decolorising agent. The ketone consists of apple-green, rhombic crystals which melt at 140—141° with the production of a deep green liquid (Found: C = 73·5; H = 5·9. $C_{19}H_{18}O_4$ requires C = 73·6; H = 5·8 per cent.).

3′ : 4′-*Methylenedioxy-2-hydroxydistyryl Ketone*.—6·5 Grams of *o*-hydroxystyryl methyl ketone and 5·9 grams of piperonal were dissolved together in 100 c.c. of absolute alcohol, and the solution was then treated with 32 c.c. of 10 per cent. sodium hydroxide solution (2 mols.). After standing thirty hours at room temperature, the mixture was diluted with ice-water and neutralised with dilute acetic acid. The bright yellow product was allowed to harden and crystallised from a mixture of alcohol and benzene. Yield (crude) 10·5 grams. For analysis, the ketone was recrystallised three times from alcohol–benzene mixture. It consists of golden-yellow needles, melting at 170—171° (slow heating) with frothing and decomposition. The compound is moderately soluble in alcohol with a yellow colour, but only slightly soluble in benzene,

the solution in this case being more nearly orange in colour (Found: C = 73·2; H = 4·7. $C_{18}H_{14}O_4$ requires C = 73·5; H = 4·8 per cent.).

2-*Hydroxystyryl Furfurylidenemethyl Ketone*,

$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O$.

—Sixteen grams of *o*-hydroxystyryl methyl ketone and 10 grams of furfuraldehyde were dissolved in 70 c.c. of absolute alcohol, and 16 c.c. of 50 per cent. sodium hydroxide solution (2 mols. NaOH) then added to the mixture. As heat was developed in the reaction, the mixture was diluted with 50 c.c. of water and cooled with ice-water. After standing over-night, the reaction mixture was poured into 700 c.c. of ice-water and neutralised with dilute acetic acid. The product, which had an ochre colour and the appearance of a solidified oil, was recrystallised from ethyl acetate, using animal charcoal. Only a small portion was thus obtained crystalline, the remainder being oily. For analysis, the crystalline product was recrystallised three times from absolute alcohol, and, finally, once from benzene, in which it is rather sparingly soluble. The ketone forms bright yellow, glistening prisms, melting at 162—163°, with violent frothing and the production of the characteristic dark green liquid (Found: C = 75·0; H = 5·1. $C_{15}H_{12}O_3$ requires C = 75·0; H = 5·0 per cent.).

New Modification of o-*Hydroxystyryl Methyl Ketone*,

$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$.

—5·4 Grams of *o*-hydroxystyryl methyl ketone and 5·1 grams of gentisaldehyde were dissolved together in 50 c.c. of absolute alcohol, and the solution was then treated with 4 mols. of sodium hydroxide (5·3 grams NaOH in 7·5 c.c. of water). After a few minutes, 10 c.c. of water were added and, shortly afterwards, a dark solid commenced to separate out. The whole was left over-night and the deep brown mixture then diluted with water and neutralised with dilute acetic acid. As very little solid separated, the solution was accordingly saturated with brine and extracted with ether. After drying over calcium chloride, the ether was distilled off and the residual oil immediately taken up in benzene. On standing, 2·5 grams of a faintly yellow solid separated out which, after twice recrystallising from boiling benzene, using animal charcoal, was obtained in long, colourless prisms, melting at 139° and showing no depression when mixed with a specimen of the original *o*-hydroxystyryl methyl ketone (Found: C = 73·9; H = 6·3. $C_{10}H_{10}O_2$ requires C = 74·1; H = 6·2 per cent.).

p-*Hydroxystyryl Methyl Ketone*.—The only method given in the literature for the preparation of *p*-hydroxystyryl methyl ketone is that of Zincke and Muhlhausen (*Ber.*, 1903, **36**, 134), who obtained

the compound in poor yield by means of acid condensation. We have now prepared this ketone very conveniently by the following method:

Four grams of *p*-hydroxybenzaldehyde were dissolved in 15 c.c. of acetone and the solution was then treated with 5·3 c.c. of 50 per cent. sodium hydroxide solution (2 mols. NaOH). Ten c.c. of water were then added and the mixture was gently warmed for a few moments. By the following day, the whole had solidified to an orange-red, crystalline mass, which was dissolved in water and decomposed with dilute hydrochloric acid, when a golden-yellow oil, which solidified on standing, separated out. The yield was practically theoretical. After recrystallisation, first from dilute acetone and then from boiling water, using animal charcoal, the ketone was obtained in long, almost colourless needles, melting at 114—115° (Zincke and Muhlhausen give the melting point as 102—103°) (Found: C = 74·0; H = 6·3. Calc., C = 74·1; H = 6·2 per cent.).

In conclusion, we desire to express our thanks to the Department of Scientific and Industrial Research for a grant to one of us (J. S. B.) which has enabled this investigation to be undertaken.

DEPARTMENT OF ORGANIC CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL. [*Received, May 16th*, 1922.]

CXXXIII.—*Studies of the Constitution of Soap Solutions. Sodium Behenate and Sodium Nonoate.*

By ORIEL JOYCE FLECKER and MILLICENT TAYLOR.

PREVIOUS communications * have been devoted to the study of solutions of salts of the saturated fatty acids containing an even number of carbon atoms, from the acetate up to the stearate. Data are now presented for sodium nonoate, as representing soaps with an uneven number of carbon atoms, and for sodium behenate with its twenty-two carbon atoms, lying almost beyond the range of the soaps proper.

Nonoic acid was chosen because it is the only acid containing an uneven number of carbon atoms which can readily be obtained in a state approaching purity. The numerical data for sodium nonoate are here found to lie between those of the octoate and the decoate, showing that the soaps of uneven carbon number

* For references, see McBain, Laing, and Taylor, this vol., p. 621.

fall regularly into the series and are intermediate in properties between the neighbouring even soaps. This is what might have been expected from the properties of such a synthetic acid as margaric acid (L. Schneider, *Dissert.*, München, 1913).

The properties of the solutions of sodium behenate present interesting and only partly investigated problems, due on the one hand to the very great possibilities of undercooling, and, on the other, to the tendency of behenate to separate from solution. The equilibria involved are, however, of the same general type as those in the ordinary soap solutions. The amount of ionic micelle in concentrated solution does not differ greatly from that in the other soaps, but neutral colloid is much more largely developed and, like the ionic micelle, persists in more dilute solution.

The data in the present paper include conductivities, osmotic activities, and densities of solutions of both soaps in addition to observations on physical behaviour.

Experimental.

The behenic acid was obtained through the kindness of Messrs. Crosfield and Sons, who made it specially by hardening Kahlbaum's erucic acid. It was purified by recrystallisation from 80 per cent. alcohol, its molecular weight as ascertained by titration before and after treatment being 343·2 and 340·0 (theory 340·3). The melting point of the recrystallised material was 81·0—82·0°. Meyer, Brod, and Soyka (*Monatsh.*, 1913, **34**, 1113) give the melting point of the purest acid they could obtain as 82—84°, but they state that if it is prepared from impure acid or left too long in contact with the catalyst, impurities, which lower the melting point but cannot be detected analytically, are obstinately retained.

Pure nonoic acid was obtained from Kahlbaum.

The experimental method for the determination of the conductivity was that used by McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179) using glass cells in every case but that of the half-normal solution.

Owing to the high viscosity of the sodium behenate solutions, it was found impossible to determine the conductivity of solutions of concentrations higher than half-normal. Even in the case of this solution (half-normal) the difficulty of forcing the dipping-electrode vessel into the liquid, and the entrapping of air bubbles which could not be removed, may have led to results which are lower than the true conductivity values. On the other hand, all solutions of sodium behenate showed a tendency to separate, even at 90°, into two distinct phases, a stringy curd and a thin, alkaline liquid.

(approximately N/20). This ready separation and the frothing of dilute solutions may account for the deviations in molar conductivity of dilute solutions of identical strength.

The densities were determined as in previous communications; each value given is the mean of two independent measurements.

The sodinm nonoate solutions were made up in silver tubes according to the method previously descrihed (T., 1914, **105**, 418), using nonoic acid "Kahlbaum." All measurements were carried out in Jena-glass vessels. *All the solutions were clear at the high temperature, although on cooling or long standing a fine sediment* always settled. This is in accordance with the observations of Bunbury and Martin (*loc. cit.*) with solutions of octoates and hexoate and is presumably due to acid soap.

Conductivity and Osmotic Data.

The conductivity results for behenates and nonoates are collected in Tables I and II, and the lowering of dew point for the nonoates in Table III. All concentrations are expressed in weight normality. Several independent solutions were studied in each case. The corresponding determinations of osmotic activity for the behenates were made and recorded by McBain and Salmon (*J. Amer. Chem. Soc.*, 1920, **42**, 426; *Proc. Roy. Soc.*, 1920, [*A*], **97**, 44).

TABLE I.

Conductivity of Solutions of Sodium Behenate at 90°.

Weight normality.	Grams of soap to 100 grams of water.	Spec. cond.	Mean.	$d_{4°}^{90°}$.	$\mu^{90°}$.
0·500	18·12	0·03469 0·03112	0·03291	0·96	80·96
0·200	7·249	0·011110 0·011325 0·01091 0·01119	0·01113	0·96312	61·99
0·100	3·624	0·005806 0·006625 0·006230	0·006244	0·9644	67·09
0·050	1·812	0·003975 0·003681 0·003528	0·003728	0·9657	78·58
0·010	0·3624	0·001184 0·001384 0·001413 0·001469	0·001363	0·96534 *	141·7

* Taken equal to that of water.

TABLE II.

Conductivity of Solutions of Sodium Nonoate at 90°.

Weight normality.	Grams of soap to 100 grams of water.	Spec. cond.	Mean.	$d_{4°}^{90°}$.	$\mu^{90°}$.
1·000	18·018	0·08794 0·08919	0·8897	0·98216	106·9
(0·500					127·5)
0·200	3·6036	0·02807 0·02826	0·02817	0·96955	150·44
0·100	1·8018	0·01582 0·01577	0·01580	0·9672 *	166·42
0·020	0·3604	0·003716 0·003664	0·003690	0·9653 *	191·82
0·010	0·1802	0·001955 0·001891	0·001923	0·9653 *	199·8

* Taken equal to that of water.

TABLE III.

Osmotic Activity of Solutions of Sodium Nonoate at 90°.

Weight normality.	$\Delta_0 C$.	Osmotic activity.
0·2	0·165	1·71
0·5	0·36	1·49
1·00	0·52	1·08

It should be noted that the osmotic activities of the nonoat solutions *are intermediate between those of the octoate and th* decoate (compare the diagrams of McBain and Salmon, *loc. cit* The conductivities are about 83 to 88 per cent. as great as tho of sodium acetate and thus fall into their expected places. Tl conductivity increases regularly with dilution.

The conductivity of the behenate exhibits a very decided minim at $0{\cdot}2N_w$. The minimum is more pronounced and occurs at slightly higher concentration than in the case of the ordina soaps, although the general form resembles that of sodi palmitate. Owing to the impossibility of extending the obser tions to high concentrations it cannot be decided whether or the conductivity would again fall off in very high concentration

At room temperature, especially after long standing, all nonoate solutions deposited a slight sediment, although the fr $0{\cdot}1N_w$-solution was clear when hot and freshly made; the N_w-s tion was clear even in the cold. The sediment is presumably soap.

The Constituents of the Solutions.

Using the methods previously described (McBain, Taylor, and Laing, *loc. cit.*) it is possible to deduce the concentrations of each of the constituents present in these solutions. The results, as calculated by Miss M. H. Norris, are shown in Tables IV and V and Figs. 1 and 2. Fig. 3 contains for comparison the results of similar measurements and calculations for solutions of potassium laurate (C_{12}).

TABLE IV.*

Concentrations in Relative Proportions of the Constituents of Solutions of Sodium Behenate at 90°.

Weight normality.	Total cryst.	Na˙.	Be′.	NaBe.	Ionic micelle.	Neutral colloid.	Acid soap.
0·01		0·005206	0·004506	0·003394	0·00	0·00	0·0021
		52·06 %	45·06 %	33·94 %			21 %
0·05		0·01508	0·013580	0·03192	0·00	0·00	0·0045
		30·16 %	27·16 %	63·85 %			9·0 %
0·2	0·19	0·047	0·028	0·115	0·019	0·035	0·003
		23·5 %	14 %	57·5 %	9·5 %	17·5 %	1·5 %
0·5	0·23	0·148	0·010	0·072	0·138	0·274	0·006
		29·6 %	2·0 %	14·4 %	27·6 %	54·8 %	1·2 %

* Acid soap is expressed in terms of behenate radicle. The allotment of total colloid between ionic micelle and neutral colloid, and of crystalloid between behenate ion and simple sodium behenate, is made in accordance with the conductivity data for $0·05N_w$-solution ($K = 0·05224$); had the conductivity for $0·01N_w$-solution been used instead, the alteration would have affected dilute solutions only, increasing neutral colloid at the expense of ionic micelle and causing it to persist in more dilute solutions. The acid soap is presumed to be similar to that of the palmitate.

TABLE V.†

Concentrations in Relative Proportions of the Constituents of Solutions of Sodium Nonoate at 90°.

Weight normality.	Total cryst.	Na˙.	Non′.	NaNon.	Ionic micelle.	Neutral colloid.
0·01		0·00862	0·00862	0·00138	0·00	0·00
		86·2 %	86·2 %	13·8 %		
0·02		0·0165	0·0165	0·0035	0·00	0·00
		82·5 %	82·5 %	17·5 %		
0·2	0·342	0·130	0·130	0·082	0·00	− 0·012
		65 %	65 %	41 %		− 6 %
0·5	0·7453	0·272	0·253	0·220	0·019	0·008
		54·4 %	50·6 %	44·0 %	3·8 %	1·6 %
1·0	1·076	0·438	0·307	0·331	0·131	0·231
		43·8 %	30·7 %	33·1 %	13·1 %	23·1 %

† The small amount of acid soap is not included in the table or the corresponding diagram. The constant used for allotting crystalloid was $K = 0·596$.

Comparison of Figs. 1 and 2 in the light of the intermediat member shown in Fig. 3 shows clearly that the difference betwee

FIG. 1.

*The relative proportions of the various constituents of solutions of pure sodiu behenate at 90°. (The asterisk * marks the field showing the proportio of acid soap, 2NaBe,HBe, present).*

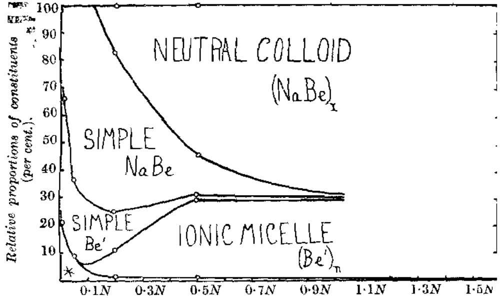
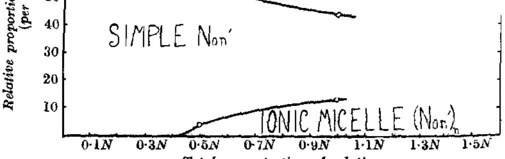


FIG. 2.

The relative proportions of the various constituents of solutions of pure sodium nonoate at 90°.



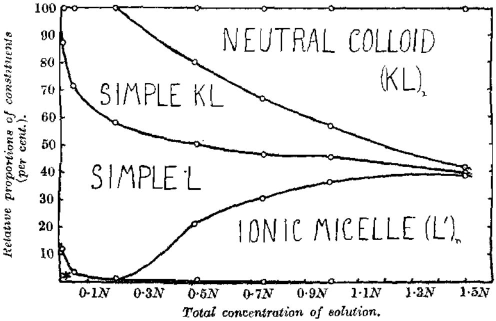
the highest and lowest salts in this homologous series is merel one of degree, exhibiting steady transition. The chief differenc

is that highly concentrated solutions of the lower members correspond with moderately dilute solutions of the highest soaps. The diagrams for the highest soaps are compressed towards the left-hand side as compared with the lower soaps, but the type remains the same.

Sodium acetate is not so highly dissociated as sodium chloride. This weakness is rapidly accentuated as the homologous series is ascended, until in the behenate the greater proportion of the crystalloidal matter is undissociated.

Fig. 3.

*The relative proportions of the various constituents of solution of pure potassium laurate at 90°. (The asterisk * marks the field showing the proportions of acid soap, 2KL,HL, present.*



There appears to be no such great difference in the amount of ionic micelle attained in concentrated solutions, although the dissociation of colloidal electrolyte into ionic micelle is unmistakably least in the highest soaps.

The most prominent effect of these relationships is that the amount of neutral colloid in ordinary solutions increases rapidly with each step in ascending the homologous series, so that, for instance, in a half-normal behenate solution the amount of neutral colloid is twice as great as in the same concentration of the palmitate (C_{16}).

There is still no very satisfactory information with regard to the effect of extremely high concentration on a soap which in moderate concentration consists entirely of neutral colloid and

ionic micelle. It is surprising that further concentration does not appear to drive back the dissociation of the colloidal electrolyte. The approximate constancy of the proportion of ionic micelle depends of course on the assumption that its mobility is likewise nearly constant. The proportion of ionic micelle becomes constant at about 40 per cent. in the laurate, at 30 per cent. in the palmitate, and at about 38 per cent. in the behenate, the remainder being neutral colloid in each case.

Appearance of Solutions of Sodium Behenate.

The curding temperature of the more concentrated solutions appears to be above 90°, although $0{\cdot}5N_w$-solution can be prepared as a clear, stiff jelly at this temperature. The liquid separating from the curd is alkaline. Hydrolysis would appear to be very much greater than has been observed in the case of any soap, and quantitative work is necessary. The solutions were increasingly opalescent on dilution, and oily drops were observed on the surface of $0{\cdot}01N$-solutions at 90°.

Remarkable behaviour is observed on rapid cooling of behenate solutions. Whereas the ordinary stable form of all except the $N_w/100$-solution is a hard, white curd at room temperature, on sudden cooling a mobile, slightly milky liquid is obtained. For instance, the slightly viscous, almost gelatinous $0{\cdot}2N_w$-solution at 90° becomes quite mobile, and this thin, cloudy, alkaline liquid may be kept for many hours before solidification occurs *; shaking causes separation of a stringy, membranous curd. A quantitative investigation of these solutions is being undertaken. Even the jellies which so readily form in these solutions have a tendency to segregate, particularly when they are agitated.

Summary.

1. Sodium behenate solutions (C_{22}) exhibit the same type of dissociation as the higher soaps such as palmitate and stearate. Although in very high concentrations of any of the soaps there is but little difference in the amounts of neutral colloid and ionic micelle, which constitute almost the whole of the solution, these persist in much more dilute solution in the case of the behenate.

2. The nonoate, as representative of fatty acids with an uneven number of carbon atoms, exhibits properties intermediate between those of the adjacent members with even number of carbon atoms.

* This observation was made by Mr. S. E. Wiltshire.

This work was carried out at the suggestion of Professor McBain, ad grants in aid were received from the Research Fund of the hemical Society and from the Colston Research Society of the Iniversity of Bristol.

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CXXXIV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part III. The Absorption Spectra of Bromomalonic Derivatives and Nitroparaffins, and their Bearing on the Question of an Oxygen–Halogen Linking.*

By HUGH GRAHAM and ALEXANDER KILLEN MACBETH.

IN previous papers (Macbeth and Pratt, T., 1921, **119**, 1356; Hirst and Macbeth, this vol., p. 904; Henderson and Macbeth, this vol., p. 892) the labile nature of the halogen atom in different types of organic compounds was studied, and it was pointed out that as there was no structure common to the representative substances of the various types examined, the chemical behaviour of the halogen atom in the different compounds could not be explained on the grounds of the presence of a particular linking. The results, moreover, seemed to be satisfactorily accounted for by a consideration of the polarities of the constituent atoms in the molecule, notably the oxygen atoms of carbonyl, ethoxyl, and nitro-groups. When viewed from this standpoint it was seen that the halogen atom in compounds which are readily acted on by reducing agents is of a strongly electropositive nature, and the chemical properties of the substances are accounted for by this characteristic factor.

It has, however, been suggested that the labile nature of the halogen atom is connected with certain structural arrangements, the reactive compounds containing an oxygen–halogen linking. This view was especially advocated by Willstätter and Hottenroth (*Ber.*, 1904, **37**, 1775), and it has also been adopted by other workers (Vorländer and Kohlmann, *Annalen*, 1902, **322**, 239). The first-mentioned workers were led to propose an oxygen–bromine linking to account for the surprising reactivity of the halogen atom in bromonitromalonic ester. Ammonia, in either alcoholic or aqueous solution, reacts briskly with the ester, forming the ammonium salt of nitromalonic ester. As this action is in strong contrast to the behaviour of bromonitroacetic ester, which is

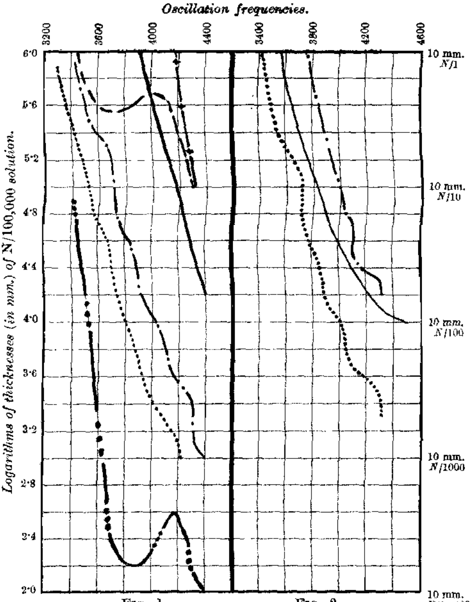

FIG. 1. FIG. 2.

FIG. 1.

——————— *Malonic ester (methyl) in alcohol.*
— + — + — „ „ „ *in water.*
— — — — „ „ „ *in* N/10-*sodium hydroxide.*
—·····— „ „ „ *in alcohol* + N/10-NaOEt.
— · — · — *Monobromomalonic ester (ethyl) in alcohol.*
· · · · · · · · · *Dibromomalonic ester* „ „

FIG. 2.

——————— *Ethyl diethylmalonate in alcohol.*
— · — · — *Monochloromalonic ester (ethyl).*
· · · · · · · · · *Methyl-, ethyl-, and propyl-bromomalonic esters in alcohol.*

gradually converted into bromonitroacetamide, it was concluded that the bromine atom in bromonitromalonic ester was linked in special way, and was, in fact, attached to an oxygen atom of

the nitro-group. This assumption is expressed in the formulæ (I) $(CO_2R)_2C{<}^{O}_{NOBr}$ and (II) $(CO_2R)_2C{:}NO{\cdot}OBr$. The labile nature of the halogen in the oxygen–halogen linking was assumed by analogy with the reactive chloro-oximes which Mohlau claimed to have isolated (*Ber.*, 1886, **19**, 280; 1887, **20**, 1504), but Ponzio subsequently showed that these substances did not exist (*Atti R. Accad. Sci. Torino*, 1906, **41**, 415, 862). Formula I was preferred on account of the decomposition which takes place when bromonitromalonic ester is heated under ordinary pressure; nitrosyl bromide is split off and mesoxalic acid formed, thus: (I) $\longrightarrow CO(CO_2R)_2 + NOBr$.

The evolution of nitrosyl bromide in the above decomposition seems a strong argument in favour of the oxygen–halogen linking, but Wislicenus and Fischer (*Ber.*, 1910, **43**, 2239), when examining the properties of *o*-bromophenylcyanobromonitromethane, found that it, like bromonitromalonic ester, decomposed on heating, nitric oxide and bromine being rapidly evolved. They prefer to regard the reaction as a liberation of nitric oxide and bromine rather than as an evolution of nitrosyl bromide, for, as little is known about nitrosyl bromide in the gaseous state and as it begins to decompose at about the boiling point (−2°), it is probable that at the temperature of the reaction mixture it would no longer exist.

Willstätter and Hottenroth adduced further support for their formula from the action of potassium iodide on bromomalonic ester. Iodine is liberated in the absence of acid, and they formulate the reaction as follows: (I) $+ 2KI \longrightarrow (CO_2R)_2C{<}^{O}_{NOK} + I_2 + KBr$. Kurt Meyer is of opinion that this reaction does not necessitate a structure involving an oxygen–halogen linking (*Ber.*, 1914, **47**, 2374). The equation above postulates a similar structure for the bromo-compound and the potassium salt, and this may readily be tested by an examination of the absorption spectra of the compounds. It has been shown that nitro-compounds containing a true nitro-group show a characteristic absorption of light, the curves displaying one or more regions of rapid extension or "kicks" (Hantzsch and Voigt, *Ber.*, 1912, **45**, 85; Harper and Macbeth, T., 1915, **107**, 87). Nitromalonic ester, bromonitromalonic ester, and nitro*iso*succinic ester (Fig. 3) all show absorption of this type, and therefore it must be concluded that the alternative formulæ, involving an oxygen–halogen linking, proposed for bromonitromalonic ester are untenable. The absorption of the potassium salt is of a type entirely different from that of the parent substance, and indicates that the structure has in this case been modified to an *aci*-form.

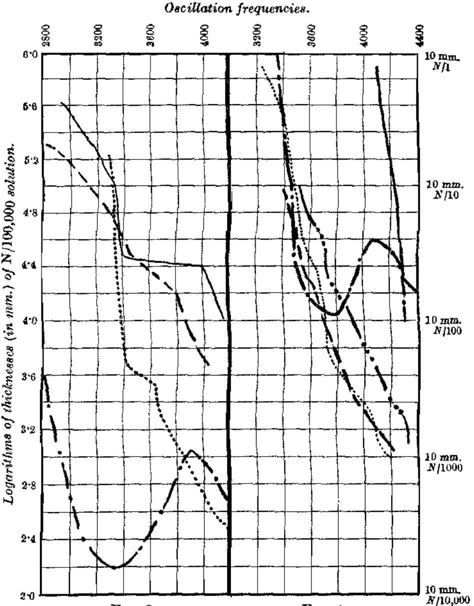

FIG. 3. FIG. 4.

FIG. 3.

———— *Nitromalonic ester (ethyl) in alcohol.*
— — — — *Bromonitromalonic ester (ethyl) in alcohol.*
. . . . *Nitroisosuccinic ester (ethyl) in alcohol.*
— · — · — *Potassium salt of nitromalonic ester in water.*

FIG. 4.

———— *Malonamide in water.*
— · — · — ,, *in N/10-sodium hydroxide.*
. . . . *Bromomalondimethylamide in alcohol.*
—···—···— *Monobromomalonamide in water.*
— — — — *Dibromomalonamide in water.*

Constitutions analogous to that proposed for bromonitromalonic ester were advanced to meet the case of the nitroparaffins containing reactive halogen atoms. A bromine atom, for example, is readily

removed by the action of alkali from dibromo- and chlorobromo-dinitromethane (Losanitsch, *Ber.*, 1882, **15**, 471; 1884, **17**, 848) and from α-bromo-αα-dinitroethane (E. ter Meer, *Annalen*, 1876, **181**, 1). Other examples of lability are found in the cases of chloro- and bromo-trinitromethane, phenylbromodinitromethane, and tetranitromethane (Macbeth and Pratt, *loc. cit.*; Baillie, Macbeth, and Maxwell, T., 1920, **117**, 880). The oxygen–halogen formulæ proposed to meet such cases are of the type $R_2C{<}^{O}_{NOX}$, where X represents a halogen atom or a nitro-group, dibromodinitromethane and tetranitromethane, for example, being represented by

$$NO_2{\cdot}CBr{<}^{O}_{NOBr} \text{ and } (NO_2)_2C{<}^{O}_{NO{\cdot}NO_2}.$$

The action of alkali on these substances, it must be supposed, would give metallic derivatives having a structure similar to those written above, and therefore the absorption spectra in the case of a bromo-compound and its metallic derivative should be of a similar type. It is known that tetranitromethane shows only the general absorption characteristic of true nitro-compounds (Harper and Macbeth, *loc. cit.*), and chlorotrinitromethane, bromotrinitromethane, dibromodinitromethane, and phenylbromodinitromethane (Figs. 5 and 6) are also found to give curves which clearly show that they contain only true nitro-groups. The corresponding salts, on the other hand, all show the characteristic absorption bands which are connected with a modified structure, or *aci*-form. The study of the absorption spectra, therefore, seems to furnish direct evidence against the existence of an oxygen–halogen linking in bromonitromalonic ester and the halogen derivatives of nitro-compounds.

It might be contended that the lability of the halogen atom in the bromomalonic esters and the bromomalonamides may be accounted for by the presence of an oxygen–halogen linking. Although the halogen atom in such compounds is supposedly attached to carbon, there is a possibility of migration to an oxygen atom with the formation of the halogen analogue of the sodium derivatives of malonic ester. The labile nature of the halogen atoms in dibromomalonic ester would thus be accounted for by a formulation, $BrO{\cdot}C(OEt){:}C{:}C(OEt){\cdot}OBr$, corresponding with that of the disodium salt (Haller and Muller, *Compt. rend.*, 1904, **139**, 1180). Considerable doubt, however, has been thrown on the existence of the disodium salt, for Vorländer showed, by molecular-weight determinations in boiling alcohol, that it behaved as a mixture of the monosodium salt with sodium ethoxide (*Ber.*, 1899, **32**, 1876; 1903, **36**, 268; see also Macbeth and Stewart, P., 1913, **29**, 11). At the outset, therefore, some doubt arises as to the

possibility of the existence of a double oxygen–halogen linking in the malonic series. The question may readily be settled by an examination of the absorption spectra of the compounds. The results obtained in such work are expressed in Figs. 1, 2, and 4. Ethyl diethylmalonate and methyl malonate show only weak

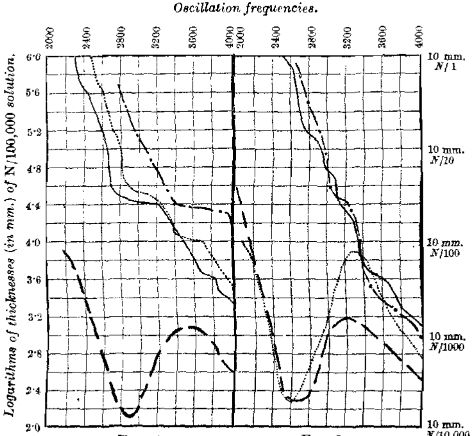

FIG. 5. FIG. 6.

FIG. 5.

———— *Bromonitroform in alcohol.*
. . . . *Chloronitroform* ,,
— · — · — *Nitroform in sulphuric acid.*
— — — — *Potassium salt of nitroform in water.*

FIG. 6.

———— *Dibromodinitromethane in alcohol.*
— · — · — *Phenylbromodinitromethane in alcohol.*
. . . . *Potassium salt of monobromodinitromethane in water.*
— — — — ,, ,, ,, *phenyldinitromethane.*

general absorption, but in the presence of alkali the latter develops a band, which has a high penetration in alcohol and a considerably lower penetration in water. This selective effect is doubtless due to the sodium derivative of the malonic ester, and its low penetration in aqueous solution is due to the easily hydrolysable nature of the salt. One is therefore justified in attributing a strong selective

effect in alcoholic solution to *O*-derivatives of malonic ester of the type XO·(OEt)C:CH·CO·OEt. The absorption curves of chloro-, bromo-, and dibromo-malonic esters and methyl-, ethyl-, and propyl-bromomalonic esters all show general absorption of the same kind as that displayed by the parent esters themselves, and it may therefore be concluded that the structure of these compounds is of the same type. An oxygen–halogen linking cannot therefore be present in the bromo-compounds.

The results obtained with the malonamides are shown in Fig. 4. In this case also the sodium derivative is characterised by a selective effect, but malonamide itself and bromomalonamide, dibromomalonamide and bromomalondimethylamide show only general absorption. The absorption spectra therefore show that malonamide and the bromo-derivatives possess similar structures, and as these differ from that of the sodium derivative, which presumably contains an oxygen–sodium linking, it seems clear that the halogen compounds are normal *C*-derivatives. In the substituted amides the absorption is somewhat more marked than in malonamide itself, but this is the expected consequence of the introduction of the halogen atom.

The absorption spectra of all the types examined furnish direct evidence against the presence of an oxygen–halogen linking in the reactive halogen compounds, and the labile nature of the halogen atom in such substances cannot therefore be accounted for on such grounds.

Norris and Thorpe (T., 1921, **119**, 1199) have dealt with the question of the oxygen–halogen linking in certain *spiro*-compounds and have disproved its existence experimentally. Representative substances of this type have been examined, and it is hoped to communicate the results obtained in a further paper.

We wish to express our thanks to Professor A. W. Stewart and the Queen's University of Belfast for access to their spectroscope.

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CXXXV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part IV. The Tautomeric Hydrogen Hypothesis, and the Removal of the Halogen Atom from Aromatic Nitro-compounds.*

By Alexander Killen Macbeth.

In previous papers (T., 1921, **119**, 1356; this vol., p. 904) the action of hydrazine on organic halogen compounds was examined; the results obtained were considered in conjunction with those observed with other reducing agents, and an explanation was put forward which seems to account satisfactorily for the different reactions (this vol., p. 892).

In a recent paper (Burton and Kenner, this vol., p. 489) the behaviour of tetranitromethane and of the halogen derivatives of nitroform has been discussed, and from a review of the cases of the substituted nitroparaffins and other examples found in the literature, these workers have been led to propose the hypothesis that the labile nature of the halogen atoms in the compounds examined by us is in some measure due to the tendency of these substances to acquire a tautomeric hydrogen atom: since, of all the substances dealt with in our first paper, the only compound which failed to react with hydrazine was bromonitromethane, which already contains the required tautomeric hydrogen atom, Burton and Kenner were led to state that "the conclusion is almost irresistible that this factor determines the reactions observed."

Thole and Thorpe (T., 1911, **99**, 2183), when studying the action of sodium ethoxide on various open-chain and alicyclic compounds containing carbethoxy-groups, found that under certain conditions a carbethoxy-group was replaced by a hydrogen atom, ethyl carbonate being formed as a reaction product. They concluded that when the terminal hydrogen atoms in systems of the type HC·C:C or HC·C:NH are all replaced "the tendency for the compound to acquire that hydrogen atom which is necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent." Although this hypothesis furnishes a good explanation of the cases considered by them, it does not appear satisfactory when applied to account for the reactivity of the halogen atom in the substituted nitroparaffins and other organic compounds.

It may rightly be contended that if a compound possesses a marked tendency to acquire a tautomeric hydrogen atom it will retain such an atom once it has been introduced into the molecule.

From this point of view bromodinitromethane furnishes a strong contradiction of the tautomeric hydrogen hypothesis, for on acidifying a solution of its potassium salt the product obtained is dibromodinitromethane, which contains no tautomeric hydrogen atom (Losanitsch, *Ber.*, 1883, **16**, 51; Wolff, *Ber.*, 1893, **26**, 2219). One of the bromine atoms in this compound is readily removed by hydrazine hydrate or potassium hydroxide solution, and the second bromine may also be eliminated by treatment with reducing agents (Duden, *Ber.*, 1893, **26**, 3004). The comparative stability of the bromine atom in the potassium salt is not to be accounted for by the presence of the tautomeric atom, but is rather to be attributed to the *aci*-structure of the salt, which has the formula $NO_2\cdot CBr{:}NO\cdot OK$.

It is evident that this substance falls into the class of compounds which contains a halogen atom joined to a carbon atom to which a double bond also is attached. Vinyl bromide and the α- and β-chloropropylenes are the best known examples of this type of substance, and the halogen atoms in these compounds are exceptionally stable, the aptitude for double decomposition being almost entirely lacking. In view of the general stability of halogens in union with a doubly-linked carbon atom, the slight reactivity of the bromine atom in monobromodinitromethane is not surprising.

Further evidence against the hypothesis that the labile nature of the halogen atom is due to a tendency of the molecule to acquire a tautomeric hydrogen atom is found in the case of the chlorosulphonamides and the halogen derivatives of malonic ester. The dichlorosulphonamides readily lose one atom of chlorine on treatment with 10 per cent. potassium hydroxide solution. The resulting potassium salt of the monochlorosulphonamide contains the required tautomeric atom, but the chlorine is readily removed from it by the action of hydrazine hydrate. As the monochlorosulphonamide salt is of an easily hydrolysable nature, the stability of the halogen atom noted in the case of compounds like monobromodinitromethane is not to be expected in this case.

The bromomalonic esters furnish perhaps the most striking examples against the tautomeric hydrogen hypothesis. The dibromo-ester reacts with hydrazine hydrate and the two halogen atoms are removed. The monobromo-ester, which contains the hydrogen atom required to allow the substance to react in its tautomeric form in the presence of alkali, is also readily acted on by hydrazine with the removal of the bromine atom. Other cases of a similar nature may be found in the bromomalonamides, etc.

The explanation which accounts most satisfactorily for the reactive nature of the halogen atoms seems to be that already advanced by us, for it differentiates between the reactivity of the

halogens themselves. Thus, *cyclo*hexane*spiro*-4 : 4-*dichlorocyclo*hexane-3 : 5-dione liberates no nitrogen from hydrazine hydrate, whereas *cyclo*hexane*spiro*-4 : 4-dibromo*cyclo*hexane-3 : 5-dione is acted on and one bromine atom removed, nitrogen being liberated quantitatively according to the equation :

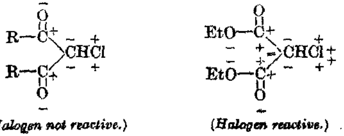
$$2C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}{>}CBr_2 + NH_2\cdot NH_2 \rightarrow$$
$$2C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}{>}CHBr + N_2 + 2HBr.$$

The halogen atom is not removed from either 3-chloroacetylacetone or 3 : 3-dichloroacetylacetone, which is in full agreement with the behaviour of *cyclo*hexane*spiro*-4 : 4-dichloro*cyclo*hexane-3 : 5-dione. On the other hand, monochloro- and dichloro-malonic esters react readily with hydrazine according to the equations :

$$2CHCl(CO_2Et)_2 + NH_2\cdot NH_2 = 2CH_2(CO_2Et)_2 + N_2 + 2HCl.$$
$$CCl_2(CO_2Et)_2 + NH_2\cdot NH_2 = CH_2(CO_2Et)_2 + N_2 + 2HCl.$$

These results all find ready interpretation when the polarities of the oxygen atoms in the molecule are considered. The negative polarities of these atoms in the two carbonyl groups endow the halogen atoms in all the above compounds with an electropositive character: and as chlorine is much more electronegative than bromine, the resultant electropositiveness in the compounds considered will be much greater in the case of the bromine atom. Thus the effect of the two carbonyl groups in the chloroacetylacetones and in the *spiro*dichloro-compound is not sufficient to make the halogens so electropositive that they will react with hydrazine: but the bromine atom, in virtue of its inherently less electronegative nature, becomes sufficiently electro-positive to decompose the hydrazine readily.

In the chloromalonic esters the effect of the two carbonyl groups is reinforced by the polarities of the oxygen atoms in the two ethoxyl groups; and the chlorine atoms are now of so electropositive a nature that they are readily removed by reducing agents.



(*Halogen not reactive.*) (*Halogen reactive.*)

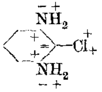
From the results now recorded and those previously obtained, it seems clear that the labile nature of the halogen atom in organic

compounds is not connected with a tendency of the substances to acquire a tautomeric hydrogen atom, but is satisfactorily accounted for by the electropositive character of these atoms.

It would appear that similar reasoning may be applied to the aromatic nitro-compounds containing halogen atoms. It was shown that the halogen atom is removed from picryl chloride during reduction with titanous chloride (this vol., p. 892), and it was pointed out that if the reaction took the course picryl chloride ⟶ chlorotriaminobenzene, the halogen atom in the latter would be of a strongly electropositive character and would be liable to removal during reduction.

Reduction with tin and hydrochloric acid also removes the halogen from picryl chloride, giving triaminobenzene (Flesch, *Monatsh.*, 1897, **18**, 757). It seemed of interest to try a method of gentle reduction in the hope of reducing the nitro-groups without the removal of the chlorine, and a catalytic reduction with iron filings and water was carried out: the halogen, however, was removed in this case also.

Consideration of the aromatic nitro-compounds from the point of view of the polarities of the groups indicates that the halogen atom is electropositive in amino-compounds which contain the amino-groups in positions ortho or para to it.



Accordingly, it is to be expected that the halogen atom will be removed from such compounds during reduction, a bromine atom being eliminated more readily than a chlorine atom. Reference to the literature shows that there is much support for this view. 1-Bromo-2 : 4-dinitrobenzene on reduction with tin and hydrochloric acid is converted into *m*-phenylenediamine (Zincke and Sintenis, *Ber.*, 1872, **5**, 792). Parallel to this is the removal of the carboxyl group from 2 : 4-dinitrobenzoic acid on reduction with tin and hydrochloric acid (Wurster, *Ber.*, 1874, **7**, 149).

The chlorine atom is not removed from 1-chloro-2 : 4-dinitrobenzene during reduction (Beilstein and Kurbatoff, *Annalen*, 1879, **197**, 76), the influence of two amino-groups not being sufficient to make it labile: and 1-bromo-2 : 4-phenylenediamine may be prepared by careful reduction of the dinitro-compound by catalytic methods (Morgan, T., 1900, **77**, 1204). Other cases of the removal of halogen during the reduction of 2 : 4-dinitro-compounds are

well known, and the conversion of 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene into *m*-phenylenediamine may be quoted as another striking example (Jackson and Calvert, *Amer. Chem. J.*, 1896, **18**, 465).

In contrast to these cases is the stability of the halogen atom during the reduction of other dinitro-compounds. Thus the halogen derivatives of *o*- and *p*-phenylenediamines are readily obtained by the reduction of the corresponding nitro-compounds (Laubenheimer, *Ber.*, 1876, **9**, 773; Witt, *Ber.*, 1874, **7**, 1604; 1875, **8**, 145; Schiff, *Monatsh.*, 1890, **11**, 338; Calhane and Wheeler, *Amer. Chem. J.*, 1899, **22**, 452).

Experimental.

Ethyl chloromalonate was prepared by the gradual addition of sulphuryl chloride (1 mol.) to ethyl malonate (1 mol.), the latter being gently warmed to start the reaction. Having been kept for some time, the mixture was heated under reflux for an hour to complete the reaction, and the product fractionated under reduced pressure; it had b. p. 118°/16 mm. and $n_D^{14°}$ 1·4363. An alcoholic solution was prepared containing 1·945 grams in 10 c.c. Two c.c. of this solution, on treatment with 50 per cent. hydrazine hydrate, liberated 23·4 c.c. N_2 at 13° and 760 mm. The bimolecular quantity (389 grams) therefore liberates 28·06 grams N_2, so the reaction takes place quantitatively in accordance with the equation already given.

Ethyl Dichloromalonate.—This is conveniently prepared by the action of sulphuryl chloride (1 mol.) on the monochloro-ester. After standing for a few days, the mixture is distilled at atmospheric pressure, the main fraction passing over at 233—234°/775 mm. It has b. p. 110°/6 mm. and $n_D^{14°}$ 1·4450. An alcoholic solution containing 1·145 grams in 10 c.c. was prepared and 2 c.c. of this solution, on treatment with hydrazine, liberated 24·5 c.c. N_2 at 13° and 730 mm. The molecular quantity (229 grams) therefore liberates 28·2 grams N_2, so the reaction proceeds according to the equation already given.

3-*Chloroacetylacetone.*—This is best prepared by the action of sulphuryl chloride on acetylacetone (Combes, *Compt. rend.*, 1890, **111**, 272), and is purified through the copper salt. The product has b. p. 155°/760 mm. and $n_D^{20°}$ 1·4784. It does not liberate nitrogen from hydrazine hydrate.

3 : 3-*Dichloroacetylacetone*, prepared by the action of sulphuryl chloride (1 mol.) on the monochloro-compound (Combes, *loc. cit.*), has b. p. 80°/12 mm. and $n_D^{20°}$ 1·4575. It is not reduced by hydrazine hydrate in the cold.

cyclo*Hexane*spiro-4 : 4-*dichloro*cyclo*hexane*-3 : 5-*dione* was prepared by Norris and Thorpe's method (T., 1921, **119**, 1199). It is not reduced by hydrazine hydrate.

cyclo*Hexane*spiro-4 : 4-*dibromo*cyclo*hexane*-3 : 5-*dione* was prepared by Norris and Thorpe's method (*loc. cit.*). 0·676 Gram was washed into a Van Slyke nitrometer with a little water and 1 c.c. of hydrazine hydrate added; 23·9 c.c. N_2 were liberated at 10° and 737 mm., so the bimolecular quantity (676 grams) liberates 28·1 grams N_2. One bromine atom, therefore, is removed in accordance with the equation already given.

Reduction of Picryl Chloride.—The picryl chloride was prepared by Jackson and Gazzolo's method (*Amer. Chem. J.*, 1900, **23**, 384). Five grams of picryl chloride and 15 grams of iron filings were gradually added to 20 c.c. of water, containing 0·5 c.c of concentrated hydrochloric acid. The acidified water was kept at 60° and the mixture was stirred throughout the reduction. When the reduction was complete, the iron was removed by filtration and well washed with hot water, the filtration and washing being done as quickly as possible. The combined filtrates and washings were acidified with concentrated hydrochloric acid, and the solvent removed by distillation under greatly reduced pressure. A mass of brown crystals was deposited on evaporation. The product was carefully and completely dried in a vacuum; the yield was more than 4 grams. On titration of an aqueous solution of the salt with standard alkali, results were obtained which agreed with the theoretical value for the trihydrochloride of triaminobenzene: 0·5 gram was dissolved in 200 c.c. of water, and 25 c.c. of the solution required 6·8 c.c. of 0·107*N*-sodium hydroxide; the purity of the triaminobenzene trihydrochloride is therefore approximately 95 per cent.

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NOTE.—Since this communication was submitted a paper has appeared (Burton and Kenner, this vol., p. 675) dealing with the elimination of the halogen atom during the reduction of halogenated aromatic nitro-compounds. The results obtained seem to be in agreement with the views expressed above, as the "experiments may therefore be said further to support the view that the removal of halogen in the reactions and conditions under consideration does not precede the formation of the amino-group."

CXXXVI.—*The Behaviour of the Stannic Acids towards Hydrochloric Acid.*

By George Ernest Collins and John Kerfoot Wood.

In a previous communication (this vol., p. 441), the authors advanced the hypothesis that the difference in the character of α- and β-stannic acids depends on the extent to which a process of condensation between molecules of stannic hydroxide has taken place, the cause of this condensation being the amphoteric nature of the hydroxide. The first step in this process of condensation was considered to be the formation of α-stannic acid, H_2SnO_3, from a single molecule of stannic hydroxide; the gradual conversion of the α-acid into the β-modification, which takes place slowly at the ordinary temperature and more rapidly on boiling, is due to the continuation of the process of condensation, thus leading, by the loss of water from several simple molecules, to the production of molecules of gradually increasing complexity and of increasing β-character. It was pointed out that the hypothesis is in harmony with numerous instances of the comparative behaviour of the two varieties of stannic acid, as recorded in the literature; in this connexion, the behaviour of the stannic acids towards solutions of strong acids and bases may be mentioned. It is well known that β-stannic acid may be converted back into the α-variety by boiling with hydrochloric acid or with solutions of alkaline hydroxides; this reversal of the α–β change, as will be shown, is quite in agreement with the authors' hypothesis. In the present paper the behaviour of the different modifications of stannic acid towards solutions of hydrochloric acid is discussed, and an account is given of results recently obtained in this field of investigation; the discussion of the behaviour of the stannic acids towards alkaline hydroxides will form the material of a subsequent paper.

Numerous observations relating to the influence of hydrochloric acid on the stannic acids are recorded in the literature. The investigations of van Bemmelen ("Die Absorption," p. 393 *et seq.*) and of Jörgensen (*Z. anorg. Chem.*, 1908, **57**, 353) indicated that the action was one involving adsorption, a definite adsorption isotherm being obtained by the former from experiments in which a uniform quantity of the so-called metastannic acid was added to hydrochloric acid solutions of varying concentration. The opinion expressed by Engel (*Compt. rend.*, 1897, **124**, 765; 1897, **125**, 464) and Kleinschmidt (*Monatsh.*, 1918, **39**, 149) to the effect that products of definite composition are formed by the action of hydrochloric acid on the stannic acids is not absolutely opposed to the

view expressed above; both investigators used stannic acid of practically the same degree of condensation, and therefore adsorption products of similar composition would be obtained.

With regard to the solubility of the stannic acids in hydrochloric acid, whilst the consensus of opinion has been to the effect that the α-modification passes into solution on treatment with either dilute or concentrated hydrochloric acid (Musculus, *Ann. Chim. Phys.*, 1868, [iv], **13**, 95; Zsigmondy, *Annalen,* 1898, **301**, 361; Kühl, *Pharm. Ztg.*, 1908, **53**, 49), it is generally stated that the β-acid is insoluble in the dilute acid, although the opposite view was upheld by Dott (*Pharm. J.*, 1908, [iv], **27**, 486).

Mecklenburgh (*Z. anorg. Chem.*, 1912, **74**, 207; 1914, **84**, 121) considered that, once the β-acid had been precipitated, it was only possible to re-obtain a sol by peptisation with concentrated hydrochloric acid for a definite time, followed by dilution; most chemists appear to have held views of a similar nature. There appears to be no obvious reason, however, why, if a stable sol is obtainable by Mecklenburgh's method, the same should not also be capable of formation by the direct action of dilute hydrochloric acid on β-stannic acid, and, as shown in the latter part of this paper, sols have been obtained by the authors in this manner, although, of course, the time required for the production of a sol, using dilute acid, is greater than that necessary when a more concentrated acid solution is employed.

The reaction between stannic acid and a solution of hydrochloric acid, as conceived by the authors, is, especially with the more highly condensed specimens of the acid, a somewhat complex process. The first stage, as observed by van Bemmelen (*loc. cit.*), is no doubt a simple adsorption of the hydrochloric acid. The amount of acid adsorbed from a solution of given concentration by a given weight of stannic acid will obviously depend on the extent of surface of the latter substance and therefore will, in accordance with the authors' hypothesis, be smaller with a sample of β-stannic acid than with one of the α-acid. To adsorb a given weight of hydrochloric acid, therefore, from a given solution, a larger weight of β- than of α-stannic acid would be required, a deduction which is in agreement with the experimental results.

Following on the adsorption, chemical action between the adsorbent and some of the adsorbed acid may take place, due to the neutralisation of the latter by some of the basic affinities of the original stannic hydroxide still possessed by the condensed acid; this will result in the formation of a certain amount of salt on the surface of the particle. Such a salt would be capable of ionisation, and would then yield a complex positive ion and chloridion. It will depend

primarily on the concentration of hydrochloric acid still remaining in solution whether or not this ionisation actually occurs; the salt and the acid give rise to a common ion, and in view of this fact and the small solubility product which the salt will have, at any rate in the case of a highly condensed stannic acid, a small concentration of acid will be sufficient to repress practically entirely the ionisation of the salt. If the ionisation of the salt is not prevented, the complex *particles will acquire a positive charge and it will depend on the ratio between its mass and the charge it carries whether or not a* particle can separate itself from adjacent ones and thus acquire a greater degree of dispersion. Owing to the greater degree of condensation and therefore the greater mass and smaller adsorptive power of the β-modification of stannic acid, it follows that this variety will not be so readily peptised as the α-acid. The latter modification will the more easily be brought into a state of true solution; with an acid of β-character, however, it may easily arise that the ratio of mass to charge is of such dimensions that the particle is not raised to the potential which will enable it to lead a separate existence, *in which case the substance will not peptise but will* remain in the condition of a gel. Conversely, *sols of* β-*stannic acid* will be more readily coagulated than sols of the α-modification, as the particles in the former sol are, for a given charge, less dispersed than those in the latter sol; this is in agreement with the measurements of the "sulphate value" of such sols made by Mecklenburgh (*loc. cit.*).

In the foregoing discussion, only one chemical action of the adsorbed hydrochloric acid and of the results arising from this reaction have been considered. It must not be forgotten, however, that the adsorbed acid may react in another manner on the stannic acid. *According to the hypothesis which has been advanced,* the more β the character of the acid, the greater is the extent to which salt formation between acidic and basic stannic hydroxide has taken place. If a highly condensed stannic acid, therefore, be in the presence of hydrochloric acid, there will be a tendency for this salt-like complex to be decomposed by the stronger acid, and by this reaction there will be formed a less condensed stannic acid. This decomposition or reversal of the α–β change will, for a given preparation, take place to a greater degree the higher the concentration of the hydrochloric acid, the longer the time of contact, and the more elevated the temperature. These deductions from the theory are supported by observations made by Barfoed (*J. pr. Chem.*, 1867, **101**, 368), Musculus (*loc. cit.*), and Mecklenburgh (*loc. cit.*).

The formation, however, of a less condensed acid will mean an increase in the surface of the particles, bringing in its train variations

in the adsorptive power and chemical affinity, both of which will entail changes in the amount of hydrochloric acid remaining in solution and in the degree of dispersion of the stannic acid.

As a result of these various changes, which, it is obvious, may take place in such a system as has been considered, it is possible to conceive that a degree of condensation of the stannic acid may eventually be arrived at which shall be in equilibrium with the free hydrochloric acid and with the substance which has been dispersed, so that no further peptisation or coagulation shall take place. Such a state of equilibrium, it would be expected, would only be attained after the lapse of a very considerable time, especially when it is remembered that certain of the reactions involved are taking place in a solid medium. During the period of attainment of this equilibrium, it would be expected that the liquid would manifest continual change of composition and that the amount of tin existing in true and in colloidal solution would also be continually changing. These expectations, it will be seen, are fully borne out by the results of the authors' experiments.

A state of equilibrium may, of course, be approached from two different directions, and it will be apparent, therefore, that the changes involved during the hydrolysis of a dilute solution of stannic chloride will be, essentially, the converse of those which have been discussed above.

EXPERIMENTAL.

It will be obvious, from the general character of the authors' hypothesis respecting the cause of the difference between the α- and β-modifications of stannic acid, that the preparation of a dry specimen of the α-variety will be quite impossible for the reason that the α–β change immediately commences and will be taking place during the whole period of drying. The utmost possible, therefore, is the preparation of a variety of the acid in which the α–β change has taken place to a limited extent and the comparison of the properties of this preparation with those shown by an acid prepared under conditions more favourable to the process of condensation, such as would be obtained, for example, at a higher temperature of preparation. For the authors' experiments, two specimens of stannic acid were prepared under different conditions, and these will, for convenience of reference, notwithstanding the above statement, be described as α- and β-stannic acids respectively.

Preparation of α-Stannic Acid.—This substance was prepared by the action of marble on a solution of stannic chloride. In order that the product obtained from different preparations should be of practically the same character, it was necessary to standardise the method of preparation.

To the solution of 500 grams of crystalline stannic chloride in 6 litres of water marble was added and the mixture kept at about 18°. The precipitated stannic acid was decanted from the undissolved marble, filtered through linen to remove as much as possible of the solution of calcium chloride, and repeatedly washed by decantation until the wash water gave no trace of opalescence on the addition of silver nitrate and was also without action on litmus and congo-red papers. The precipitate was removed by filtration through linen and was then placed on porous plates and allowed to dry in air. After about a month from the commencement of drying the substance had changed to a dark brown, vitreous, semi-transparent product; the substance was coarsely powdered and the air-drying continued, the substance being weighed from day to day. When the daily loss of weight had assumed small dimensions the acid was finely powdered, sieved through No. 10 flour silk, and the drying allowed to proceed to completion; a period of fifteen days elapsed between the attainment of the vitreous stage and the completion of the drying process.

On ignition, the air-dried product was found to contain 79·6 per cent. of stannic oxide, which gave the gel a composition of $SnO_2,2{\cdot}14H_2O$.

The α-stannic acid was, in spite of the prolonged washing, not quite free from chlorine. The amount of chlorine present was found to be 0·16 per cent., the analysis being made by peptising a given weight of the acid with potassium hydroxide, acidifying with nitric acid, and estimating the chlorine by the Volhard method; a blank determination, using similar quantities of alkali and nitric acid, was conducted in order to avoid any inaccuracy which might otherwise arise because of the presence of traces of chlorine in the materials used.

As anticipated, the preparation was not of true α-nature, it not being dissolved to any appreciable extent by either dilute or concentrated hydrochloric acid. On treatment with the concentrated acid, followed by dilution with water, it peptised, but was reprecipitated on the addition of a further amount of the concentrated acid.

Examined under the high power of a microscope (magnification about 350), the substance appeared glassy and transparent, but non-crystalline. On ignition, a pale yellow oxide was obtained; this oxide was found to be slightly hygroscopic, the amount of water taken up on exposure to air amounting to 0·25 per cent.

Preparation of β-Stannic Acid.—This was the so-called metastannic acid. One litre of pure concentrated nitric acid was heated in a flask of about 4 litres capacity until the liquid began to boil, when

the source of heat was removed and 100 grams of granulated tin were added within the space of about two minutes. After the cessation of the initial violent reaction, the mixture was heated for some time on the water-bath to ensure the solution of any particles of unchanged metal. After cooling, the supernatant acid liquid was syphoned off and the residue was then repeatedly washed by decantation with boiling distilled water until the washings gave no reaction for nitrates with a solution of diphenylamine in sulphuric acid. The acid was then separated by filtration through linen, dried on porous plates, and sieved, as described in the preparation of the α-variety. As might be anticipated from the more granular character of the preparation as compared with the somewhat gelatinous precipitate obtained in the preparation of the α-modification, the drying of the β-stannic acid required a considerably shorter time than was necessary in the case of the α-acid. The proportion of water in the air-dried β-acid was somewhat smaller than that contained in the α-modification, the average composition being expressed by $SnO_2,1{\cdot}91H_2O$. The smaller amount of water in the substance indicates that the α–β change has proceeded to a greater extent than in the case of the product which has been designated α-stannic acid.

Under the microscope, the β-acid presented an appearance very similar to that of the α-modification. In view of the presence of chlorine in the α-acid, it was thought desirable to submit the β-acid to further examination for traces of nitric acid. Following the method used by Zsigmondy and Heyer (*Z. anorg. Chem.*, 1910, **68**, 169) for the detection of traces of chlorides in silicic acid, the product was distilled with concentrated sulphuric acid until the latter substance itself began to come over, the distillate being received in a solution of diphenylamine in sulphuric acid; no evidence of the presence of even a trace of nitric acid was obtained in this way.

Action of Hydrochloric Acid on the Stannic Acids.

The same principle was adopted in these experiments as in the determination of the solubility of a substance, although, of course, the results obtained do not correspond with actual solubilities. Successive amounts of the α- or β-acid were added to the solution of hydrochloric acid until some of the solid was apparently unacted on; no further addition was made until the stannic acid previously added had disappeared. The mixtures, which were contained in flasks made of resistance glass, were kept in a thermostat maintained at 25° and periodically examined; occasional analyses of the liquids, which will be described later, were made. In a second series of experiments the stannic acid was first treated with concentrated

hydrochloric acid and then diluted with water; if, after some time, no precipitation took place, a further addition of stannic acid was made and the mixture then left for a considerable period before any analysis was undertaken.

The two modifications of the acid did not behave in the same manner when added to solutions of hydrochloric acid, the changes observed with the β-acid being of a more striking character than those manifested by the α-variety. In the cold of the former, the finely powdered substance first caked together and later became yellow and semi-transparent; at this stage it began to disperse gradually into the liquid above it. The changes mentioned took place the more rapidly (i) the greater the hydrochloric acid concentration (within the limits studied), (ii) the smaller the amount of stannic acid already peptised.

In the case of the α-acid the preliminary caking was noticed on several occasions, but in no case was there any formation of the semi-transparent, yellow product. It is worthy of note that the changes observed with the β-acid do not occur when that substance is treated with a saturated solution of hydrochloric acid in dry benzene, the substance showing no change of appearance after a period of four months. The material had, however, adsorbed a considerable quantity of hydrochloric acid, for the concentration of the latter compound in the solution had fallen, and the solid itself, when added to water, yielded an opalescent liquid which gave a white precipitate on the addition of concentrated hydrochloric acid. It appears probable that the formation of the semi-transparent yellow product is due to imbibition of some of the aqueous solution prior to actual peptisation, and that it is not observed with the α-acid owing to the latter being more readily peptised.

In both series of experiments it was observed that an increase in the amount of β-stannic acid added to a given volume of hydrochloric acid led to the mixture becoming more and more viscous and eventually becoming a stiff gel, which, in some cases, could be broken up only with difficulty by shaking.

In general, the α-sols were much clearer than the analogous ones obtained with the β-acid. The sols appeared yellowish-orange when viewed by transmitted light; seen by reflected light, the α-sols appeared faintly green and the β-ones bluish-white. In the case of the β-mixtures, the similarity in the appearance of the yellow semi-transparent gel already mentioned and of the yellow supernatant liquid was particularly striking.

A few typical records of the behaviour of the two varieties of stannic acid when added to solutions of hydrochloric acid of varying

concentration are given in Table I. In every case the volume of acid employed was 200 c.c. The figures illustrate the difference between the quantities of the two modifications which could be added to acid of about the same concentration before apparent saturation resulted, as well as the dependence of the rate of peptisation on the concentration of the hydrochloric acid and on the amount of stannic acid already added.

TABLE I.

Variety of acid.	Normality of HCl.	Stannic acid added (grams).	Behaviour.
α	0·197	2·50	No change during 196 days.
α	0·620	7·50	After 105 days very faintly collodial; no further change.
α	1·033	10·00	Dispersed after 7 days.
		2·00	Dispersed after 17 days more.
		more added	Remained undissolved.
β	0·197	1·00	No change during 196 days.
β	0·591	10·00	Opalescent after 13 days; after 107 days heavily colloidal; no further change; solid faintly yellow.
β	1·102	5·00	Became yellow in 2 days and dispersed into liquid in 4 days.
		10·00	Dispersed into liquid after additional 22 days.
		20·00	Did not completely disappear; after 67 days viscous and after 81 days coagulated.
β	1·50	5·00	Dispersed in 1 day.
		,,	Dispersed in about the same time.
		,,	Dispersed in 2 days.
		,,	Dispersed in 2 days.
		,,	Dispersed in 3 days.
			Further large additions were required, the mixture becoming more and more viscous and finally coagulation took place.

In Table II are given a few examples of observations made in the second series of experiments, in which the stannic acid was peptised with concentrated hydrochloric acid and the mixture then diluted until the volume became 200 c.c. An interesting feature of these results is that they show that a stannic acid sol may be coagulated by the addition of further quantities of stannic acid; the latter fact does not appear to have been previously observed.

Methods of Analysis.—As already mentioned, analyses of the various mixtures prepared were made from time to time, the particular object in view being the detection of any changes in the composition of the sols with increasing age. An attempt was made not only to measure such changes of composition, but also to determine whether there was any alteration in the proportion o

TABLE II.

Variety of acid.	Approx. normality of HCl after dilution.	Stannic acid added (grams).	Behaviour.
a	0·3	3·00	*On dilution gave opalescent solution. After 19 hours a heavy turbidity and partial deposition of gel, and in 4 days the liquid contained much white precipitate. After 187 days the mixture, when shaken, appeared like a colloidal solution.*
a	0·9	9·00	On dilution gave opalescent solution. After 16 days all had dispersed.
		2·00	40 days after this addition all had dispersed.
		more	Remained undissolved after 90 days.
β	0·3	2·50	Similar to that recorded above for *a*-acid.
β	0·9	20·00	On dilution gave opalescent solution, which gradually became more cloudy. After 12 days dispersed.
		10·00	7 days after this addition the solid was yellow and semi-transparent and the liquid very opalescent. After 63 days the liquid contained thick gel. After 87 days lumps of undispersed yellow gel and of coagulated white gel in colloidal liquid; white gel dispersed on shaking.

material present in the colloidal and in the molecular condition. The following method was employed in order to determine these various values. A portion of the contents of the flask in question was filtered through a single No. 50 Whatman filter-paper (with the aid of the pump if necessary). This filtrate was taken as containing all dispersed stannic acid, whether present in the colloidal or molecular condition; a portion of it was therefore retained for analysis and the remainder submitted to ultra-filtration in order to determine the amount of tin in the molecular state. In order to secure uniformity in the collodion membranes employed for ultra-filtration, the necessary nitrated cotton was prepared in the laboratory by a standard method and the thoroughly washed and dried material dissolved in a mixture of alcohol and ether in the proportions to give a 2 per cent. solution. Films prepared by the slow evaporation of 30 c.c. of this solution in a petri dish of 9 cm. diameter were employed for the ultra-filtration, the films being placed, when most of the solvent had evaporated, on the top of an ordinary funnel and the edges of the film pressed down against the outer surface of the funnel; the combination of film and funnel prepared in this way was found to be vacuum tight when almost dry. The ultra-filtrates obtained by the use of such films were absolutely clear. An ex-

amination by means of the ultra-microscope showed a complete absence of individual particles.

The amount of tin in the filtrates and ultra-filtrates was determined by reduction of a given volume of the solution by means of pure aluminium foil and concentrated hydrochloric acid, followed by titration with a standard iodine solution in an atmosphere of carbon dioxide; to ensure accuracy, blank determinations were performed with similar quantities of aluminium and acid.

The amount of hydrochloric acid in solution was determined by titration with standard sodium hydroxide, using methyl-orange as indicator, whilst the total amount of chlorine ion in the liquids was estimated by Volhard's method.

The results obtained with α- and β-stannic acids respectively are given in Tables III and IV, the concentrations of hydrogen ion and of chloride ion being expressed in normalities and the concentration of tin in gram-molecules of stannic oxide per litre of solution. Those mixtures marked with an asterisk were prepared by treating the stannic acid with concentrated hydrochloric acid and diluting with water.

TABLE III.

	Filtrate.				Ultra-filtrate.			
Flask No.	Days from start.	$H^{\cdot}$.	Cl'.	SnO_2.	Days from start.	$H^{\cdot}$.	Cl'.	SnO_2.
45*	145	0·285	0·300	0·0135	140	0·291	0·299	Zero
	182	0·310	0·321	0·0005	182	0·282	0·289	Zero
16	133	0·385	0·390	0·0002	133	0·394	0·393	0·0003
	184	0·380	0·386	0·0002	175	0·380	0·391	0·0003
46*	145	0·451	0·459	0·0271	137	0·442	0·462	0·0012
	182		0·460	0·0105	181	0·444	0·468	0·0017
17	132	0·577	0·578	0·0247	132	0·588	0·583	0·0094
	183	0·596	0·605	0·0741	179	0·580	0·610	0·0229
47*	145	0·634	0·609 ?	0·202	137	0·587	0·655	0·0118
	182	0·662	0·707 ?	0·0900	183	0·603	0·624	0·0101
	206		0·653	0·0233				
18	132	0·720	0·726	0·257	132	0·675	0·666	0·0302
	184	0·737	0·740	0·241	179	0·664	0·671	0·0162
48*	145	0·736	0·740	0·290	135	0·729	0·756	0·0355
	182	0·739	0·759	0·308	179	0·671	0·731	0·0241
19	132	0·890	0·939	0·441	132	0·815	0·815	0·0655
	184	0·907	0·947	0·639	176	0·779	0·789	0·0404
49*	145	0·931	0·931	0·354	135	0·890	0·966	0·139
	182	0·934	0·992	0·883	182	0·752	0·779	0·0701
					206	0·763	0·788	0·0463

Discussion of Results.

The figures obtained show that only those mixtures in which the concentration of hydrochloric acid was of the dimensions of approximately 0·4N were apparently at equilibrium, and in those mixtures

TABLE IV.

	Filtrate.				Ultra-filtrate.			
Flask No.	*Days from start.*	*H˙.*	*Cl′.*	*SnO₂.*	*Days from start.*	*H˙.*	*Cl′.*	*SnO₂.*
12	134	0·197	0·203	0·00003				
	175	0·195	0·202	0·000035	175	0·193	0·199	0·00003
44*	145	0·302	0·294	0·0692	140	0·286	0·311	Zero
	185	0·314	0·331	0·0019				
11	135	0·391	0·392	0·0012	133	0·398	0·416	0·0004
	175	0·392	0·397	0·00044	175	0·386	0·396	0·00006
43*	141	0·474	0·501	0·0428	133	0·489	0·482	0·0023
	178	0·504	0·516	0·168	178	0·460	0·466	0·0027
2	119	0·484		0·0011	119	0·481		0·0015
	167	0·477	0·505	0·0058	161	0·487	0·527	0·0023
10	135	0·575	0·568	0·0861	133	0·579	0·578	0·0083
	175	0·569	0·575	0·0881	175	0·576	0·578	0·0068
42*	145	0·610	0·620	0·125	134	0·610	0·619	0·0078
	187	0·680	0·730	0·111	185	0·561	0·578	0·0061
3	124	0·698		0·245	119	0·646		0·0170
	166	0·704	0·733	0·278	161	0·674	0·693	0·0175
	245	0·708	0·732	0·283	239	0·735	0·748	0·0130
9	119	0·738	0·771	0·332	119	0·749	0·746	0·0183
	175	0·771	0·793	0·308	175	0·691	0·697	0·0178
41*	141	0·778	0·743	0·455	133	0·723		0·0209
	176	0·802	0·804	0·496	176	0·703	0·722	0·0162
5	156	0·913	0·983	0·784	150	0·850	0·889	0·0435
	239	0·932	0·968	0·761	233	0·780	0·788	0·0287
40*	141	1·213	1·277	0·912	133	0·900	0·923	0·0456
	178		1·266	0·660	173	0·912	0·918	0·0478
					98	1·010		0·189
6	158	1·174	1·208	1·239	153		1·020	0·0973
	241	1·282	1·356	1·090	236	0·969	1·030	0·0649
7	91	1·31		1·210	91	1·290		0·260
	149	1·433	1·525	1·680	149		1·130	0·112
	240	1·425	1·507	1·220	235	0·980	1·010	0·0802

the amount of stannic acid dispersed was of negligible dimensions. It appears, in fact, that a certain minimum concentration of hydrochloric acid (0·4—0·5*N*) is necessary before any appreciable amount of either α- or β-stannic acid is dispersed. The latter conclusion is in harmony with the fact that stannic hydroxide is stronger as an acid than as a base, and in its general aspects bears a resemblance to the results obtained by one of the authors (T., 1908, **93**, 411) from measurements of the solubility of arsenious oxide in water and in hydrochloric acid.

With regard to the composition of the filtrates, some of these showed an increase in the amount of tin dispersed with increasing time, whilst others showed a decrease in the tin content of the liquid the greater the age of the mixture. It was noticed, however, that the latter behaviour was shown by those mixtures in which gel formatio

had commenced, and a change of this kind would obviously lead to a reduction in the amount of tin in the liquid. It appears probable, therefore, that the two kinds of behaviour alluded to represent two stages which, given sufficient time, might be realised for all the mixtures, namely, a gradual increase in the amount of tin dispersed until the liquid acquires a concentration at which gel formation commences, when the tin content of the liquid will begin to fall; the results obtained with flask 7, in which gel formation was observed one hundred and seventy days from the commencement of the experiment, support this view. As regards the ultra-filtrates, the composition of these also showed changes in both directions, although the decrease in the tin content was the more noticeable phenomenon; it is worthy of note that this decrease in the amount of tin in the ultra-filtrate was sometimes observed even while the tin content of the filtrate was increasing. These changes in the composition of the ultra-filtrate are probably principally due to the slow hydrolysis of the tin compound at first present in true solution, this hydrolysis being facilitated by the changes in the liquid arising from gel formation.

It will be observed that in the majority of cases the concentration of hydrion and of chloridion in the ultra-filtrates was lower than in the corresponding filtrates; this is accounted for by the fact that the ions in question are adsorbed by dispersed particles of stannic acid contained in the filtrate but not present in the ultra-filtrate. The analyses also show that in some of the filtrates the concentration of hydrochloric acid increased with the increasing age of the mixture, but this behaviour is easily explainable. The stannic acid first adsorbs hydrochloric acid, thus reducing the original concentration of the latter in the liquid; as the stannic acid peptises, however, it carries with it the adsorbed acid, causing, therefore, an increase in the concentration of hydrochloric acid in the solution with increasing age of the mixture.

College of Technology,
Manchester. [*Received, March 21st, 1922.*]

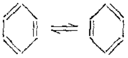
CXXXVII.—*The Structure of the Benzene Nucleus. Part I. Intra-nuclear Tautomerism.*

By Christopher Kelk Ingold.

In approaching the question of the constitution of the benzene nucleus it is essential to recognise that the best criterion of the truth of any suggested structure is its bearing on the problem of the

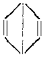
unification of the essential reactions and basic general principles of *the two main branches of organic chemistry*. This attitude is fundamental to the argument outlined below.

Hitherto the aliphatic and aromatic branches of organic chemistry have remained virtually distinct, each the field of operation of its own general laws, and the older conceptions embodied in Kekulé's dynamic formula (I), Thiele's half-valency formula (II), and Armstrong and Baeyer's centric formula (III) leave the problem of collation practically untouched; indeed, the centric formula definitely places benzene beyond the reach of any conceptions which could be evolved solely by the study of aliphatic compounds.


(I.)

(II.)

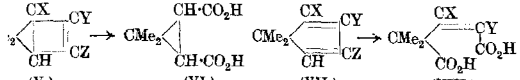
(III.)


(IV.)

Considerable historical interest attaches to formula IV, which was first suggested by Dewar (*Proc. Roy. Soc. Edin.*, 1866—1867, 84) as one of seven possible formulæ for benzene. Another of the seven was the ordinary Kekulé formula, proposed by Kekulé in 1865 and reported on to the British Association by Dewar in 1868 (*Rep. Brit. Assoc.*, 1868, 34), after Dewar himself had become acquainted with Körner's position theory. It is perhaps remarkable that Dewar's bridged formula (IV) has never gained any considerable measure of acceptance; indeed, it seems never to have been seriously considered in relation to the chemistry of aromatic compounds, although Kauffmann has employed it in the development of his theory of fluorescence (*Ahrens's Vortrage*, 1908, **12**, 35). Baeyer did not regard the bridged formula as a possibility worth examining at any period during his experimental researches, and in Richter's "Organische Chemie" (edition 1909—1913) no mention is made of it even in connexion with obsolete formulæ such as those of Claus and Ladenburg. Yet it is the purpose of this paper to show that Dewar's formula, considered in relation to present-day conceptions of carbon tautomerism, is the clue to the constitution of the aromatic nucleus.

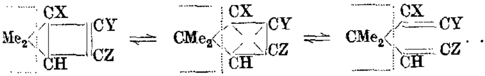
In the first place, it is necessary to refer to certain aliphatic bridged-ring compounds which appear to occupy a position in the systematic description of organic compounds intermediate between the aliphatic and the aromatic series. It has been shown (Farmer and Ingold, T., 1920, **117**, 1362) that certain acids containing a bridged *cyclo*pentane ring behave under the influence of particular reagents as though they possessed, not a bridge, but an endocyclic double bond; or, as it is equally correct to say, certain monocyclic

ısaturated compounds behave *towards some reagents as though* ıey contained a bridge-bond similar in many respects to the para-)nd in formula (IV). The same compound may be oxidised (as ıough its constitution were represented by *formula V) to a cyclo*-ropane derivative (VI), and also (as if its structure were expressed y formula VII) to an unsaturated open-chain acid (VIII) :



(V.) (VI.) (VII.) (VIII.)

Now the investigation of these bridge-bonded compounds is obviously of great importance for the understanding of aromatic character, and *the significant fact in this connexion is that both* formulæ (V) and (VII) are necessary to explain the reactions of the substance ; for recent investigation has shown (Farmer, Ingold, and Thorpe, *this vol., p. 128) that all these compounds have a* dual set of properties. The view which has been adopted, and which appears to be the only one capable of explaining the facts, is that the types (V) and *(VII) are merely phases of a state of tautomerism involving* valency exchange across and within the *cyclo*pentane ring. The two individuals, it will be observed, are valency isomerides and no *transmigration of a* hydrogen *atom occurs*. The *process is represented* thus :

 . . (*A*.)

(V.) (Transitional phase.) (VII.)

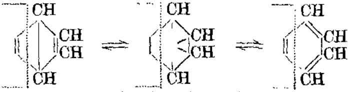
the " centric " phase, for which no direct chemical evidence exists, being inserted to aid visualisation of this intra-annular valency-exchange and to represent some uncomprehended intermediate condition which must occur, however transiently, at some moment during the transformation.

It is obvious that this phenomenon, which has been termed " intra-annular tautomerism," and has been strikingly confirmed by more recent experiments, must, if it is true, permeate every field of organic chemistry in which cyclic compounds are met with, and, in particular, must be fundamentally concerned in the production of aromatic character. Now for several years past, and on quite other grounds (below), the author has held the view that the true conception of the benzene molecule is a dynamic one, in which the

bridged phase (IV) occupies a position intermediate between the two *double-bonded phases* (I):

(I.) (IV.) (I.) . . . . . (*B*.)

We know that a bridge-bond, equally with a double bond, is invariably a point of unsaturation, so that each of these three phases consists of an endless (or closed) chain of unsaturated elements. Let us isolate from this double equation the right-hand member only, and expand it by introducing a formula for the transitional state; we obtain in this way equation (*C*), in which the analogy (confining attention for the moment to the right-hand sides of the dotted lines) with the tautomerism of the five-carbon rings (equation *A*) is very striking:



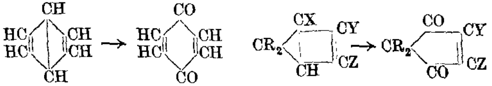
(IV.) (Transitional phase.) (I.) . . (*C*.)

The complementary transformation involving the portion of the ring to the left of the dotted lines is that corresponding with the left-hand member of equation (*B*) and is exactly similar. In short, the five-carbon intra-annular transformation constitutes a simple model illustrating the rearrangement of half the benzene ring.

However, such an analogy, although striking and valuable as confirmation, proves nothing, and the contention which has been made clearly requires the strongest possible supporting evidence. In the following parts of this series it is proposed to submit new experimental evidence bearing on the question; the purpose of the present communication is to indicate by some typical illustrations the manner in which certain classes of known fact confirm the view which has been adopted.

Probably the most characteristic, unique, and most extensively observed type of change which aromatic compounds undergo is the benzenoid–quinonoid transformation. None of the formulæ I, II, III, possesses as part of its face value any feature which clearly suggests the remarkable prevalence and the uniqueness of this change. Plainly, however, the introduction of the bridged phase brings this transformation exactly into line with those reactions which result in the formation and fission of bridge-bonds in the aliphatic series; no other formula can do so. Many reactions of benzene and its substitution products are reactions of the bridged form; many are

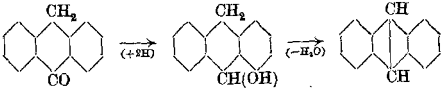
reactions of the double-bonded form. For instance, the electrolytic oxidation of benzene to *p*-benzoquinone is a reaction of the bridged phase, and is exactly analogous to the oxidation, recently accomplished, *of a bridged tautomeric individual* of type V to a cyclic 1 : 4 diketone :



The oxidation of quinol to benzoquinone is caused by the addition of two hydroxyl groups at the bridge :

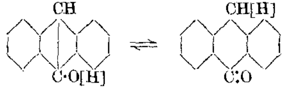
These instances are typical of a very large family of reactions in which para-quinonoid structures are produced by oxidation or by additive reactions. It seems scarcely necessary to add that the changes which result in the formation of ortho-quinonoid structures are reactions of one or other of the double-bonded (Kekulé) phases of the aromatic complex (*B*).

With regard to the formation of benzenoid compounds from quinonoid, it is to be remarked that whenever the elements of water, hydrogen bromide, *etc.*, can be *eliminated from the* 1 : 4-*positions* of a para-quinonoid substance a benzenoid structure is produced, usually with quite remarkable ease; in fact, it is generally impossible to isolate substances capable of undergoing this reaction owing to the facility with which it occurs. An illuminating instance is the reduction of anthrone to anthracene; here the primary reduction product, although very unstable, can be isolated, and, on loss of water, passes into anthracene :

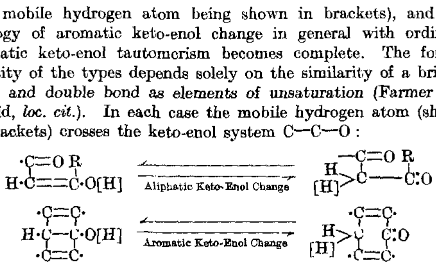


The establishment of para-linkings by this means, and the extraordinary ease with which the changes take place, find exact parallels in a number of instances of the formation of bridge-linkings across a *cyclo*pentane ring. These cases are discussed in the paper previously referred to (Farmer, Ingold, and Thorpe, *loc. cit.*), and it is only necessary to notice here that none of the substances undergoing the reaction could be isolated owing to the facility with which it took place.

Interchange between benzenoid and para-quinonoid systems can take place, however, not only by addition and by elimination of groups, but even by tautomeric interchange, and this circumstance constitutes one of the strongest reasons why the recognition of this bridged phase of the benzene nucleus is essential for the collation of the properties of aromatic compounds with known facts relating to the aliphatic series. For instance, the tautomerism of anthrone with anthranol (K. H. Meyer, *Annalen*, 1911, **379**, 39, 43) remains inexplicable and uncollated by the general theory of keto-enol tautomerism as developed by the study of aliphatic substances unless a bridged phase for anthranol be assumed. If, however, we may suppose that anthranol reacts in its bridged form, then the change can be expressed as follows: *



(the mobile hydrogen atom being shown in brackets), and the analogy of aromatic keto-enol change in general with ordinary aliphatic keto-enol tautomerism becomes complete. The formal identity of the types depends solely on the similarity of a bridge-bond and double bond as elements of unsaturation (Farmer and Ingold, *loc. cit.*). In each case the mobile hydrogen atom (shown in brackets) crosses the keto-enol system C—C—O:

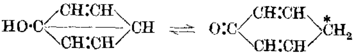


In the same way, the formation of quinonoid structures from aromatic amines by reversible isomeric change falls within the category of imino-ename tautomerism, since here the mobile hydrogen atom passes across the system C—C—N.

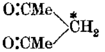
"Coupling" reactions are evidently bound up with the phenomenon of tautomerism in a very intimate manner, and form another striking illustration of collation with the aliphatic series on the basis of a bridged phase of the benzene nucleus. Phenol, for instance, condenses with diazonium salts through its bridged form, the ketonic (or anthrone-like) modification of which (related to the bridged

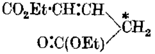
* A paper on tautomerism which involves the opening and closing of simple four-carbon rings will shortly be published.

individual much as ethyl acetoacetate is to ethyl β-hydroxycrotonate) is constituted absolutely analogously to those compounds of the aliphatic series which show corresponding properties :†



Phenol.

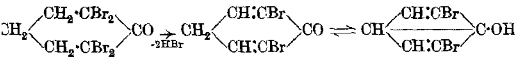




Acetylacetone. *Ethyl glutaconate.*

(Coupling position marked *.)

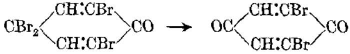
Baly and Ewbank supposed, in order to account for the absorption spectrum of phenol, that this substance exhibits tautomerism and contains a mobile hydrogen atom (T., 1905, **87**, 1347). The analogy with anthranol (p. 1138) suggests that phenol, although, of course, it is practically completely enolic, should be capahle of exhibiting mobility of the kind shown in the equation above, and, indeed, there is much chemical evidence available which proves that the para-interchange postulated can and does occur in phenol itself and its derivatives. For instance, Wallach found (*Annalen*, 1905, **343**, 42) that tetrabromo*cyclo*hexanone, when warmed alone, lost two molecules of hydrogen bromide. The product should be an unsaturated ketone, which, according to the view under discussion, is the ketonic modification of the bridged phase of 2 : 6-dibromophenol :



As a matter of fact, the product was ordinary 2 : 6-dibromophenol, showing that conversion from the keto to the enol form by the movement of a hydrogen atom across the six-carbon ring actually does occur. This is but one of many instances which might be cited. Tautomerism, however, is reversible isomeric change, and it is necessary, therefore, to show that the retrograde transformation, that is, from the enol form to the keto-form, can also take place. One instance of the occurrence of this change is furnished by the formation of 2 : 4 : 6-tribromophenol bromide from phenol

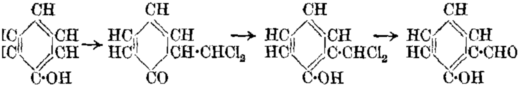
† Without doubt it is the enolic (or phenolic) form which actually undergoes the condensation (compare K. H. Meyer, *Ber.*, 1921, **54**, [*B*], 2265); nevertheless the substituted phenol thus formed can pass into its ketonic modification, which accounts for its apparent identity with the quinonephenylhydrazone. Similar considerations apply to the reaction between phenol and nitrous acid.

and bromine water. The constitution of this bromide has been established by Thiele and Eichwede (*Ber.*, 1900, **33**, 673), who have converted it into 2 : 6-dibromobenzoquinone by warming with aqueous lead acetate :

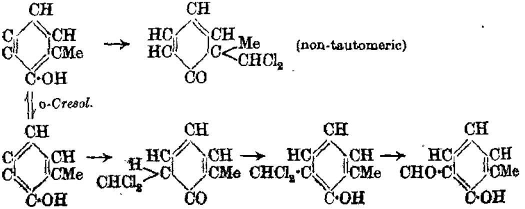


The bromide, therefore, is the tetrabromo-derivative of the ketonic modification of phenol, and its production must at some stage have involved tautomeric conversion of the (bridged) enol form into the keto-form.

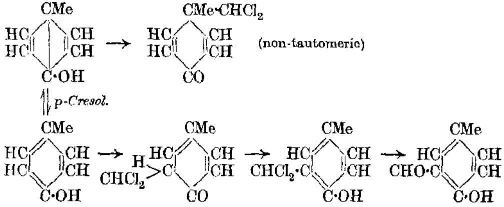
Phenol, however, may also exhibit the kind of keto-enol tautomerism which corresponds with the ordinary double-bonded formula for that substance, and it is this property which doubtless determines the course pursued by the Reimer-Tiemann reaction. Alkylation occurs on carbon as follows :



That this is so is proved by the fact that *o*-cresol, which, like all orthodisubstituted benzenes, has two double-bonded forms, gives, when condensed with chloroform, two products, one corresponding with each of the Kekulé forms of o-cresol. One of these products is a homologue of salicylaldehyde, but the other is a ketone, which, owing to the position of the methyl group, contains no mobile hydrogen atom and cannot revert to an enolic (phenolic) condition. Therefore, the general course of the series of reactions which would have taken place in other circumstances is, in this instance, arrested with the formation of a substance the constitution of which clearly reveals the mechanism of the change :



In the case of *p*-cresol, there are two forms only which are capable of undergoing tautomeric change of the keto-enol type: one is double-bonded and the other is bridged. If these two forms be examined in relation to their ability to enter into condensation with chloroform, it is at once observed that in this instance it is the condensation of the bridged modification which must be arrested after the initial stage owing to the absence from the initial condensation product of capacity for tautomerism:



Actually this is what occurs (Auwers and others, *Ber.*, 1905, **38**, 1693, and earlier) and it is difficult to imagine a satisfactory alternative explanation.

A large class of reactions in which the properties of the bridged phase of the aromatic nucleus are manifested is that group of irreversible isomeric changes which lead ultimately to substitution in the para-position. A well-known instance is the conversion of methylaniline into *p*-toluidine. The simplest assumption which one can make as to the mechanism of this change, indeed of all reactions of this type, is that they take place through the bridged phases of the initial and final products.

Many conflicting views have been expressed regarding the mechanism by which substituents in general enter the benzene nucleus, but that which seems to have gained the greatest measure of acceptance, and which is certainly the simplest and most rational, is that, in general, addition to one of the double bonds of a Kekulé phase is the first stage, and that the elimination of water, hydrogen bromide, etc., is a subsequent occurrence. Hollemann ("Die direkt Einführung von Substituenten in den Benzolkern") has stated this hypothesis in very clear terms, and has further supposed that the directive influence of groups is to be attributed to their increasing or decreasing the reactivity of the adjacent double bonds. Here, however, a difficulty is encountered in connexion with the necessity for bringing ortho- and para-substitution within the same scheme. This difficulty Hollemann endeavours to meet by introducing a

somewhat unsatisfactory assumption in which the Thiele hypothesis * is employed in a highly artificial manner, but from the preceding discussion it will be plain that the recognition of the bridged form of the aromatic nucleus as an essential phase of the complete tautomeric scheme obviates the necessity for any such supposition. One must indeed assume that those groups (the ortho- or para-directing groups) which enhance the reactivity of the adjacent double bond also favour that bridged phase in which the bridge is attached to the carbon atom carrying the group. This, however, seems probable on general grounds, for such groups would enhance the reactivity of an adjacent bridge-bond, and thus render the bridge phase more prone to yield evidence of its existence by entering into chemical reactions. It is well known, moreover, that groups, such as hydroxyl- and amino-groups, which favour conversion by oxidation or isomeric change into quinonoid structures invariably have ortho- and para-directing properties. Phenol, for instance, has two principal phases, one double-bonded and one bridged, and the nitration of phenol, therefore, yields a mixture of ortho- and para-isomerides because the first stage of the process consists in the addition of the groups $HO—NO_2$ to the activated double bond of one phase and to the bridge-bond of the other.

In the case of compounds containing substituent groups which decrease, or, at any rate, do not enhance, the reactivity of the adjacent double bond (or bridge-bond) it is probable that the most vulnerable of all the possible phases is the bridged form containing a bridge-bond between two carbon atoms other than that which bears the substituent. In certain cases, however, meta-substitution may proceed through the double-bonded phase in accordance with the mechanism suggested by Hollemann (*loc. cit.*).

These, however, are amongst the many matters which will have to be settled in the future by *experimental* investigation, for it is plain that once the broad principle outlined in this communication is accepted the whole field, not only of benzene derivatives, but also of naphthalene, anthracene, pyridine, and acridine derivatives, indeed of all aromatic compounds, lies before us, and much carefully planned experimental work is required. It has been stated, however, that quite apart from such new proof as can be obtained from specially devised experiments, the general hypothesis requires definite support from the mass of known facts relating to the aromatic series. Certain directions in which supporting evidence may be obtained have been indicated above, but it is not the purpose of the present paper to deal with this aspect of the subject even moderately completely. It is desired rather to adumbrate

* A paper dealing with this subject will shortly be published.

by means of a few chosen examples the manner in which some degree of preliminary justification of what appears to be a reasonable working hypothesis is to be sought, and in which the theoretical origin of the experiments described in the following series of papers was actually reached.

The author owes to the kindness of Sir James Dewar the information contained on p. 1134 regarding the early history of the benzene formula.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7. [Received, January 21st, 1922.]

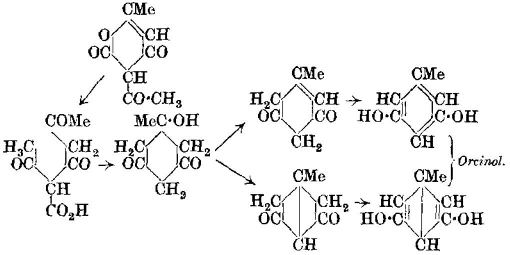
CXXXVIII.—*The Structure of the Benzene Nucleus. Part II. Synthetic Formation of the Bridged Modification of the Nucleus.*

By CHRISTOPHER KELK INGOLD.

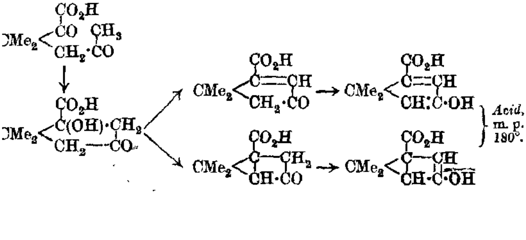
IT has been suggested that the clue to the constitution of the benzene nucleus is to be found by recognising a certain bridged structure, composed of two *cyclo*butene rings, as an essential phase of the tautomeric system of which the nucleus consists, because by making this assumption a very far-reaching collation of the characteristics of benzene derivatives with known phenomena relating to the aliphatic series can be secured, and a great diversity of facts rendered coherent and intelligible. That so wide a collation should flow from such a simple assumption seems to be the strongest justification for its introduction. Nevertheless, the matter is an important one, and therefore it appeared highly desirable to carry out certain experiments specially designed with the object of attacking the subject from such a totally different point of view that any evidence obtained, if confirmatory, would be correspondingly convincing. Several methods of approaching the problem are occupying attention, but in the present paper it is proposed to consider only the evidence provided by certain synthetic experiments which have confirmed in an interesting and singular manner the hypothesis proposed.

The benzene nucleus has been built up from aliphatic compounds in a great variety of ways, very few of which, however, can be termed rational syntheses, if by that is meant that some definite structure is indicated. Even if we leave entirely out of account condensations in which six, three, or two molecules take part (for example, the formation of benzene from six molecules of methane, of mesitylene from three of acetone, or of pyromellitic acid from two of αβ-dibromoglutaric acid), and consider only those internal

condensations in which the aromatic nucleus is produced from a single system of six carbon atoms, it would appear that the vast majority of these give ambiguous indications. Take, for example, the formation of orcinol (3 : 5-dihydroxytoluene) from dehydracetic acid (Collie and Myers, T., 1893, **63**, 124). The initial stages of the reaction, which takes place in the presence of concentrated alkali, are easily understood: they consist in the fission of the δ-lactone ring, the loss of a carboxyl group as carbon dioxide, and an internal aldol condensation. It will be noticed, however, that there are two ways in which the elements of water can be eliminated from the aldol condensation product: one way leads to the Kekulé formula for orcinol, the other to a bridged structure, which, according to our hypothesis, is merely a phase of the nuclear tautomerism of that substance:

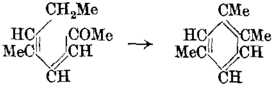


This type of ambiguous synthesis appears to be characteristic of many substances which show intra-annular tautomerism. The instance just given is in every way analogous to the formation of the *dicyclo*pentane acid (m. p. 180°) from diketodimethylhexoic acid by internal condensation (Toivonen, *Annalen*, 1919, **419**, 176; Farmer and Ingold, T., 1920, **117**, 1362; Farmer, Ingold, and Thorpe, this vol., p. 128):



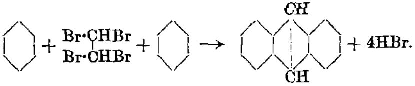
and the comparison forms a remarkable illustration of the singularly close analogy between the aromatic nucleus and the homocyclic nucleus present in the simplest known cases in which intra-annular tautomerism is exhibited.

Several syntheses, however, have been accomplished in which the kind of ambiguity illustrated by the preceding instances does not arise, and it is a curious fact that all these point unmistakably to the double-bonded form of the nucleus as the form actually produced by synthesis. One example is provided by the formation of ψ-cumene from the condensation product of α-methyl-β-ethylacraldehyde and acetone (Barbier and Bouveault, *Compt. rend.*, 1895, **120**, 1420).

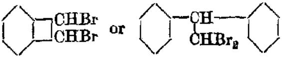


ψ-Cumene.

Therefore, in spite of the difficulty of interpreting many of the reactions by means of which the aromatic nucleus has been produced, the double-bonded formula for benzene receives from synthetic experiments the full measure of the support which they are capable of affording. The same is not true of the bridged formula. Certainly anthracene has been obtained from benzene and acetylene tetrabromide by condensation in the presence of aluminium chloride (Anschütz and Eltzbacher, *Ber.*, 1883, **16**, 623), and it is very difficult to formulate this reaction unless it is assumed that the central benzene ring of the anthracene molecule is produced in its bridged modification :



Nevertheless, it is impossible to dogmatise regarding the course followed by the condensation if for no other reason than that as many as three molecules take part in it. Unfortunately, the reaction has never been conducted in stages; it has not been shown, for instance, that any structure such as



is formed intermediately. For this reason it appeared desirable to institute a series of experiments with the object of achieving a rational synthesis of the bridged form of the aromatic nucleus; and, because, for some singular reason, the bridged formula for anthracene (above) seems to require less defence against convention than the bridged formula for benzene itself, it was determined to evolve a synthesis of some simple and typical benzene derivative, rather than of a substance containing a compound nucleus such as that of anthracene. Should the bridged-ring substance produced in this manner be found to be isomeric and not identical with the expected aromatic compound, the whole theory would be finally and completely disproved. If, on the other hand, it should be found to be identical, then the synthesis, taken in conjunction with the mass of evidence provided by the characteristic reactions of the aromatic series (Part I), would, because of its independent character, go far to establish the truth of the basic hypothesis. The essential point of the scheme was, of course, to conduct the process in successive stages, and, in particular, to close the two *cyclo*butene rings in separate operations. It will be recollected that the five-carbon ring structures (above) exhibiting intra-annular tautomerism were originally synthesised by Perkin and Thorpe (T., 1901, **79**, 729) by a method which plainly indicated the bridged constitution of the substance produced: the associated *cyclo*butane ring was closed by an internal (Dieckmann) condensation of a *cyclo*propane derivative containing a suitable side-chain:

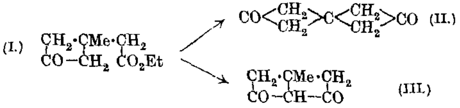
$$CMe_2{<}\begin{matrix}C(CO_2Et)\cdot CH(CO_2Et)_2\\ CH\cdot CO_2Et\end{matrix} \rightarrow CMe_2{<}\begin{matrix}C(CO_2Et)\cdot CH\cdot CO_2Et\\ C(CO_2Et)\cdot CO\end{matrix} + EtOH$$

It seemed, therefore, that if a *cyclo*butene derivative with an appropriate side-chain could be prepared, it should be possible to close the second ring in a similar manner and thus obtain a double-ring structure, which, according to our hypothesis, is the bridged modification of the benzene nucleus.

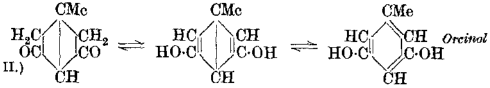
The great difficulty which has delayed the carrying out of this interesting experiment has been the difficulty of preparing a suitable *cyclo*butene compound; for nearly three years all efforts in this direction met with complete failure. Recently, however, it has been found possible to isolate from amongst the products of the action of sodium on ethyl β-methylmethanetriacetate a *cyclo*butanone ester (I) which readily undergoes the required Dieckmann reaction with the elimination of ethyl alcohol.

There are two possible ways in which this reaction might occur: one leads to the production of a spiran ketone (II), and the other to

formation of a bridged-ring ketone (III). Actually the con-

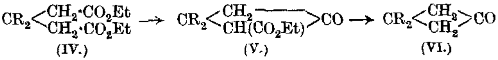


nsation takes the second course to the complete exclusion of the st. The bridged ketone (III) is, clearly, the ketonic form of the idged modification of orcinol:

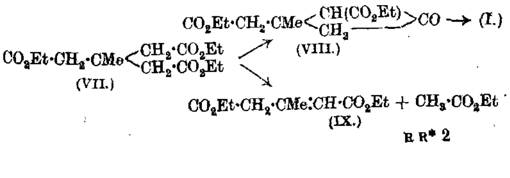


he product of the reaction was, in fact, identified as orcinol, not ıly by direct comparison with a specimen of that substance, but lso by the preparation of various characteristic derivatives.

With regard to the method by which the ketone (I) was obtained may be pointed out that Kon has recently shown (this vol., . 513) that *cyclo*butanones of type VI may be produced by he Dieckmann method from esters (IV) of substituted glutaric cids in yields of about 1 per cent. at best, but that in all probability



much larger quantities of the ketonic esters (V) are originally formed, although they are for the most part converted into reduction products by the nascent hydrogen generated. Now the yield of the ketonic ester (I) is extraordinarily small, and for two main reasons. The first is connected with the reversibility of the Michael reaction (Ingold and Powell, T., 1921, **119**, 1976). Under the experimental conditions employed a large proportion of the ethyl β-methylmethanetriacetate (VII) breaks down into ethyl acetate and ethyl β-methylglutaconate (IX). In the initial stages, therefore, there are two competing reactions, and it is probable also that the ketonic



ester (VIII) is converted by the nascent hydrogen into reduction products analogous to those obtained by Kon (*loc. cit.*), although no definite experimental evidence on this point could be obtained. The *second main cause which contributes to the smallness of the* yield of the ketonic ester (I) is the reactivity of this substance. The ring closure by means of which it is converted into orcinol takes place with much greater ease than the original ring closure involved in its formation. Consequently such ketonic ester as is formed is largely converted into orcinol (which can be isolated if the conditions are favourable), or into substances derived from orcinol by certain deep-seated reactions which this compound appears prone to undergo under the conditions of the condensation.

In conclusion, the author would like to guard himself from the imputation that he supposes the production of a typically aromatic compound, such as orcinol, by a rational double-ring synthesis to be *proof* of the existence of the bridged individual in the tautomeric system of which the aromatic nucleus consists. No single experiment or set of experiments can prove such a thing; cumulative evidence alone can do so. Nevertheless, the value of cumulative evidence depends chiefly on its diversity, and therefore it is hoped that, when considered in connexion with the testimony afforded by the characteristic transformations of aromatic compounds, the synthetic experiments will provide a strong foundation for the claim to consideration of the basic hypothesis.

EXPERIMENTAL.

The β-methylmethanetriacetic acid (ββ-dimethylpropanetricarboxylic acid) required for these experiments was prepared by hydrolysing the condensation product of labile ethyl β-methylglutaconate and ethyl sodiocyanoacetate as described by Thorpe and Wood (T., 1913, **103**, 1579). In preparing large quantities of the acid, however, it was found convenient to omit the separation of the condensation product into neutral and acid fractions and the purification by fractional distillation of the neutral cyano-ester. The alcoholic solution in which the condensation had taken place was poured into dilute hydrochloric acid, and extracted with ether. The extract was evaporated without drying, and the syrupy residue, after heating for a short time at 100° under diminished pressure, was hydrolysed with sulphuric acid. The greater portion of the triacetic acid produced was readily obtained in a condition of purity by crystallisation from concentrated hydrochloric acid, and the ultimate residues were purified by esterifying and fractionally distilling the ethyl esters, but this process yielded only a small additional amount of material.

Ethyl β-Methylmethanetriacetate (VII).—β-Methylmethanetriacetic cid gives a poor yield of the triethyl ester when digested with ulphuric acid and ethyl alcohol in the usual manner, but may be sterified almost quantitatively by the following method. The acid 00 grams) was mixed with 1 litre of absolute ethyl alcohol and 00 c.c. of concentrated sulphuric acid in a flask fitted with a short actionating column and a condenser. A current of alcohol vapour as passed into the flask, which was heated in such a way that the vel of the liquid remained unchanged. When 10 litres of distillate ad been collected in the course of five hours, the contents of the lask were cooled and poured into water, and the ester was extracted ith ether, washed with aqueous sodium carbonate, and, after emoving the ether, distilled under reduced pressure. The ethyl -methylmethanetriacetate obtained was a colourless, mobile oil, b. p. 185—187°/22 mm. (Found: C = 58·3; H = 8·4. $C_{14}H_{24}O_6$ requires C = 58·3; H = 8·3 per cent.). The yield was almost theoretical.

Action of Sodium and Potassium on Ethyl β-Methylmethanetriacetate: Formation of Ethyl 3-Methylcyclobutan-1-one-3-acetate (I), Orcinol (III), Ethyl β-Methylglutaconate (IX), Ethyl Acetate, Ethyl Acetoacetate, and corresponding Acid Products.

The Dieckmann reaction as applied to ethyl β-methylmethanetriacetate was carried out in a great variety of ways with the object of obtaining a satisfactory yield of ethyl 3-methyl*cyclo*butan-1-one-3-acetate. Although this end was not achieved, the following two processes were evolved.

(i) *Condensation by means of Sodium.*—To finely divided sodium (20 grams), prepared under hot xylene (200 c.c.), ethyl β-methylmethanetriacetate (60 grams) was added, and the mixture heated at 140°. The reaction soon commenced and proceeded with gradually increasing vigour to a point at which it was not necessary to apply heat in order to maintain the temperature. The flask was then removed from the oil-bath, kept until the vigour of the reaction began to abate, and then, although much sodium remained unattacked, immersed in cold water to check further action. The excess of sodium was decomposed by adding ice and water (the flask being fitted with a valve to prevent ingress of air), and the mixture extracted with ether (neutral extract). The aqueous portion was acidified with hydrochloric acid and again extracted with ether, the extract being washed several times with aqueous sodium carbonate (quasi-acid extract). The combined alkaline washings were acidified with hydrochloric acid and again extracted (acid extract).

The neutral extract contained ethyl β-methylglutaconate, ethyl

acetoacetate, ethyl 3-methyl*cyclo*butan-1-one-3-acetate, and ethyl β-methylmethanetriacetate. The acid fraction contained normal β-methylglutaconic acid, β-methylmethanetriacetic acid, acetic acid, and some syrupy material which was not identified.

The quasi-acid fraction gave a brown gum from which no crystalline solid could be obtained. It appeared to form neither a semicarbazone nor a *p*-nitrophenylhydrazone, and although it reacted with bromine and with acetyl chloride, no crystalline derivative could be prepared. The gum gave an intense indigo-blue colour with aqueous-alcoholic ferric chloride; however, it contained no appreciable quantity of orcinol, and indeed the colour was much more permanent than the colour given by orcinol. Experiments made with the object of determining to what extent orcinol is stable under the conditions of the condensation indicated that it is moderately rapidly converted into a gum which in the course of the separation passes into the quasi-acid fraction, and which has properties very similar to those of the gum just described.

(ii) *Condensation by means of Potassium.*—Finely divided potassium (34 grams), prepared under well-dried xylene or petroleum (b. p. 130—140°), was treated with ethyl β-methylmethanetriacetate (60 grams). No reaction occurred, even when the mixture was heated to the boiling point of the solvent, provided the materials were quite pure and dry; but on adding one drop of alcohol a violent reaction took place, the potassium dissolving with the sudden liberation of a large amount of hydrogen. When the reaction had finished, water was added (the potassium having entirely vanished), and the mixture acidified with 100 c.c. of concentrated hydrochloric acid and extracted with ether. The extract was shaken with a total quantity of 200 c.c. of 20 per cent. aqueous potassium hydroxide, and then washed once with water (neutral extract). The alkaline solution was rendered acid by adding 100 c.c. of concentrated hydrochloric acid, and again extracted with ether, and the extract washed several times with 10 per cent. aqueous sodium carbonate (first quasi-acid extract). The alkaline washings were extracted with ether (second quasi-acid extract), then acidified by adding hydrochloric acid and again extracted with ether (acid extract).

The neutral extract contained ethyl β-methylglutaconate, ethyl acetoacetate, and ethyl β-methylmethanetriacetate. The substances present in the first quasi-acid fraction were not identified. The second quasi-acid fraction contained orcinol and unidentified substances, and the acid fraction normal β-methylglutaconic acid, β-methylmethanetriacetic acid, and acetic acid.

Ethyl Acetoacetate.—The neutral fractions from the condensations

in which sodium was employed, on distillation under diminished pressure, yielded a considerable amount of ethyl β-methylmethanetriacetate together with a more volatile liquid. The volatile fractions derived from a large number of experiments were combined, and refractionated, and in this way separated almost completely into two portions, one of which boiled constantly at 85—87°/25 mm. and the other at 127—130°/20 mm. The former was identified as ethyl acetoacetate by analysis (Found: C = 55·2; H = 7·8. Calc., C = 55·4; H = 7·7 per cent.) and by conversion into 1-phenyl-3-methylpyrazolone, which was directly compared with an authentic specimen.

Ethyl β-Methylglutaconate (IX).—The fraction, b. p. 127—130°/20 mm., was unsaturated and on analysis gave figures corresponding with ethyl β-methylglutaconate (Found: C = 60·3; H = 8·2. Calc., C = 60·0; H = 8·0 per cent.). On hydrolysis with hydrochloric acid, it yielded *normal* β-*methylglutaconic acid* (m. p. 149°).

A considerable quantity of this ester had been collected during the course of these experiments before it was discovered that despite its constant boiling point and correct empirical composition it contained an appreciable amount of a ketonic ester which did not appear to be capable of being separated by distillation. Ultimately, however, the ketonic ester was isolated as described hereunder. The recovered ethyl β-methylglutaconate boiled at 132—133°/24 mm. (Found: C = 60·1; H = 8·1 per cent.).

The condensations in which potassium had been used yielded very little neutral fraction. However, when a quantity sufficient for distillation had been accumulated, it was found to consist principally of ethyl β-methylglutaconate together with a small "low" fraction, which must have contained ethyl acetoacetate since 1-phenyl-3-methylpyrazolone was obtained from it, and a "high" fraction consisting of ethyl β-methylmethanetriacetate. The ethyl β-methylglutaconate gave the less fusible form of β-methylglutaconic acid (m. p. 149°) on hydrolysis by hydrochloric acid.

*Ethyl 3-Methyl*cyclo*butan-1-one-3-acetate* (I).—The liquid of b. p. 127—130°/20 mm. (above) was treated with an aqueous solution containing equivalent quantities of hydroxylamine hydrochloride and sodium hydroxide and the whole shaken at frequent intervals during a period of forty-eight hours. An excess of sodium hydroxide was then added and the mixture again shaken. The aqueous layer was then separated, rendered faintly acid, and extracted with ether. The undried extract was evaporated, the gummy residue warmed with 20 per cent. hydrochloric acid to 80° until no further formation of oil occurred, and the oil extracted with ether, the extract being washed with aqueous sodium carbonate, dried, and evaporated.

The residue boiled constantly at 130—131°/24 mm. (Found: C = 63·5; H = 8·3. $C_9H_{14}O_3$ requires C = 63·5; H = 8·2 per cent.).

The sodium carbonate washings were acidified and the acid products extracted with ether; the viscous syrup thus obtained deposited in the course of time a little crystalline matter, but the quantity was so small that separation did not appear feasible.

Ethyl 3-methyl*cyclo*butanoneacetate is a colourless, mobile liquid, the odour of which is to be described as fruity rather than ketonic. It appears to condense with the usual reagents for ketones, but its most characteristic property is the ease with which it can be converted into orcinol (see below).

A characteristic p-*nitrophenylhydrazone* is formed when equivalent amounts of the ketonic ester and *p*-nitrophenylhydrazine are boiled together in alcoholic solution. It crystallises from alcohol in brick-red, feathery needles, which melt and decompose at 175° (Found: C = 59·4; H = 6·5. $C_{15}H_{19}O_4N_3$ requires C = 59·0; H = 6·2 per cent.).

Acetic Acid, Normal β-Methylglutaconic Acid, and β-Methylmethanetriacetic Acid.—The acid products obtained from the condensations, whether sodium or potassium was used, always set to a pasty mass in which acetic acid was recognisable by its odour. β-Methylglutaconic acid and β-methylmethanetriacetic acid were readily separated by triturating the mass with concentrated hydrochloric acid, draining on porous porcelain, and then fractionally crystallising from this solvent.

β-Methylglutaconic acid, which is less soluble than β-methylmethanetriacetic acid in concentrated hydrochloric acid, was identified by its melting point (149°), by analysis (Found: C = 49·7; H = 5·6. Calc., C = 50·0; H = 5·6 per cent.), and by direct comparison with a genuine specimen.

It is much less wasteful to esterify the pasty mass with ethyl alcohol, under the conditions described on p. 1149. From the esters a volatile fraction was obtained, which was identified by its boiling point and odour (it was not analysed) as ethyl acetate. The remainder was easily separated into ethyl β-methylglutaconate (b. p. 134—135°/25 mm.) and ethyl β-methylmethanetriacetate (b. p. 187—189°/24 mm.), both of which were identified by hydrolysing them to the corresponding acids.

Orcinol (III).—As already explained, orcinol may be obtained from the products of the action of potassium on ethyl β-methylmethanetriacetate. It crystallises from the second quasi-acid fraction, and may be purified by first draining as completely as possible on porous porcelain, and then crystallising from a small

mount of water, from which it separates as the monohydrate, m. p. 57° (Found: C = 59·1; H = 7·1. Calc., C = 59·1; H = 7·0 per cent.).

The conversion of ethyl 3-methyl*cyclo*butan-1-one-3-acetate into orcinol takes place with great ease when a solution of the ester in dry ether is added to a suspension of finely divided sodium in benzene. Two atoms of sodium were taken for each molecule of the ester, and the mixture was heated for a short time to ensure the destruction of the last traces of metal. Water was then added, and, after the neutral products had been removed by extraction with ether, the aqueous liquid was saturated with carbon dioxide and again extracted with ether. This extract on evaporation left a residue, which immediately solidified and was found to consist principally of orcinol. It was purified by crystallisation from water and was identified by its melting point (57° in the hydrated form, 102° when anhydrous), by analysis (Found: C = 59·0; H = 7·1. Calc., C = 59·1; H = 7·0 per cent.), by the ferric chloride and fluorescein reactions, by direct comparison with a genuine specimen kindly lent by Dr. M. A. Whiteley, and by the preparation of the mono-, tri-, and penta-bromo-derivatives, which had the melting points recorded in the literature. The yield was 50 per cent. of the theoretical.

These experiments were commenced in 1919 in the laboratories of the Cassel Cyanide Company, Limited, Glasgow. The author desires to thank the directors of that firm for the facilities for private research which they so kindly afforded him.

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CXXXIX.—*Some Properties of Hydrogen Desorbed from Platinum and Palladium.*

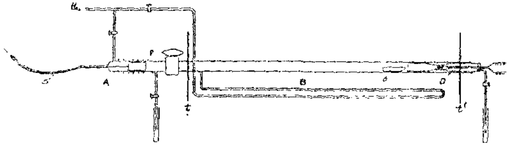
By PAUL ANDERSON.

THE contact action of the platinum metals in catalysing hydrogenation reactions has been exhaustively studied since the time of Döbereiner. Of the abnormal activity of the hydrogen in the absorbed or "combined" state there can be no doubt. Is this activity completely and instantaneously lost on desorption, or does it have a finite period of decay? This question would appear to be of some theoretical and technical interest and an attempt has been made to investigate it.

EXPERIMENTAL.

A series of preliminary experiments was first carried out with the object of establishing a difference, if any existed, between the minimal reduction temperature of copper oxide as brought about on the one hand by ordinary pure hydrogen and on the other by hydrogen desorbed from an adjacent mass of platinised asbestos. An ordinary electric tube furnace was employed, the copper oxide and platinised asbestos being contained in small quartz combustion boats. The temperature of the furnace was raised very slowly through a rheostat, and the temperature at which reduction began in each case roughly determined by the condensation of moisture in the cold delivery tube. The results obtained with this apparatus were inconsistent but of sufficient promise to warrant the construction of a modified form of apparatus insuring exact temperature

FIG. 1.



control, a highly purified hydrogen supply, and a delicate moisture detector.

For the sake of clearness in description, this apparatus may conveniently be divided into four integral parts: the hydrogen purification train, the chamber for preheating and purification of the catalytic mass from adsorbed foreign gases (*A*, Fig. 1), the reaction tube with its thermostat (*B*), and the moisture detector (*D*). The hydrogen purification apparatus presents no distinctive features and is not incorporated in the sketch. The hydrogen, obtained variously from a Kipp generator, an electrolytic barium hydroxide cell with nickel electrodes, and cylinders supplied by the British Oxygen Co., was purified first by passage through two Emmerling towers charged with solid potassium hydroxide, by which the carbon dioxide, halogens, and most of the moisture were removed. The gas was then passed through cocoa-nut charcoal cooled in liquid air for the removal of any traces of oxygen present, and finally through another tower of potassium hydroxide followed by a phosphoric oxide tube.

The chamber, *A*, and reaction tube, *B*, consisted of the arms of a large glass stopcock, which served to connect or isolate the sections

at will. The bore of this stopcock was made equal to that of the arms—in this case 2 cm.—thus permitting the unobstructed movement of the glass capsule, *p*. This capsule contained the catalytic mass of platinised asbestos and was moved from without by means of an attached piano-wire passing out through the mercury seal, *S*. The preheating chamber was wound with resistance wire, by means of which its temperature conld be gradually raised to about 300°. This section was also supplied with an inlet tube leading to the hydrogen supply and an outlet through a phosphoric acid trap.

The reaction tube, *B*, containing the copper oxide boat, *o*, in the position shown, was immersed in an electrically heated oil-bath thermostat subject to exact temperature control through an electric thermo-regulator. Thorough circulation of the bath was obtained in the usual manner by the use of a motor-driven agitator. The thermostat is diagrammatically indicated in the sketch by the heavy lines *tt'*. The purified hydrogen enters the reaction tube only after passing through a preheating worm immersed in the thermostat bath, insuring a uniform temperature throughout.

The moisture detector adopted after some experiment with various devices depended for its action on the change in the electrical resistance of anhydrous calcium chloride in the presence of slight traces of water vapour. The gas stream, after passing over the copper oxide, was concentrated by a constriction in a short glass tube fitting into the reaction tuhe as shown, and made to impinge on a globule of anhydrous calcium chloride bridging a 1 mm. gap between the ends of two parallel copper wires. A rubber stopper fitted to the outside end of the short tube served to support the wires together with the outlet tube. The Cu–$CaCl_2$–Cu resistance element was connected as the "unknown resistance" in an ordinary Wheatstone bridge apparatus. The element was prepared for use by momentarily immersing the wire ends in molten calcium chloride and replacing the wires in the tube while still hot. Since the element was placed in position only while a stream of extremely dry hydrogen was flowing through the reaction tube and before the temperature had been raised near the reduction point of the copper oxide, the calcium chloride cooled in the anhydrous state and, on balancing, the bridge was found to have a resistance of the order of 30,000 ohms. At the first incipient reduction of the oxide, with the consequent formation of a minute quantity of water vapour, the resistance of the element suddenly dropped to the order of a few hundred ohms. This drop was always sharp and unmistakable, and formed the basis of the minimal reduction temperature observations.

The description of the apparatus is suggestive of the procedure

of the determinations, which were made, in brief, as follows : The capsule containing the platinised asbestos remained in chamber *A* with the stopcock closed while a stream of purified hydrogen was passed both through *A*, which was heated at 250—300°, and through *B* at room temperature. After the sweeping-out process had continued for some time, the moisture detector was "loaded" as previously described and the temperature of the thermostat gradually raised until the drop in the resistance of the calcium chloride element indicated the initial reduction of the copper oxide. The thermostat was then allowed to cool to about 50° without interrupting the flow of gas. After the calcium chloride cell had recovered its high resistance, the capsule of platinised asbestos, which had by this time been thoroughly freed of all foreign gases and been allowed to cool to room temperature, was pushed into the reaction tube until some 3—5 mm. distant from the copper oxide boat. The stopcock was then closed after unhooking and withdrawing the wire. The temperature of the thermostat was then again raised and the reduction temperature determined as before.

The results of three typical determinations follow :

Exp.	*Minimal Reduction Temp.* Control.	Pt. adjacent.
1	103·5°	81·0°
2	115·0	86·0
3	110·5	87·0

The copper oxide employed, it may be mentioned, was precipitated in asbestos fibre after a method recommended by Sir Robert Robertson for the preparation of a catalytically active oxide.

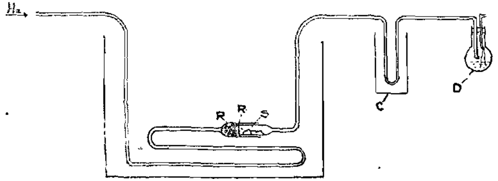
The results of the determinations never checked closely, a consequence of the variability in the activity of the copper oxide, but the differences observed between the "control" and "platinum adjacent" experiments were always marked and appear to indicate a certain increase in the activity of the desorbed hydrogen.

In order to determine the duration of the activity the thermostat was held constant at 90° and the capsule containing the platinised asbestos very gradually moved toward the copper oxide boat. Reduction was found to take place when the capsule had reached a distance of about 8 cm. from the copper oxide. The rate of flow of the hydrogen was held at 180 bubbles per minute during these tests.

With the object of obtaining further evidence by an independent method, a suggestion made by Professor E. C. C. Baly, of the University of Liverpool, was followed up and a series of determinations of the minimal reduction temperature of sulphur by normal and desorbed hydrogen made, using palladium-black as the activat-

g agent. The hydrogen purification apparatus used in the previous periments was again employed. A capillary grid or worm served preheat the hydrogen to the temperature of the palladium-black ntact mass (*P*, Fig. 2) and sulphur *s*. The short tube containing e sulphur was fitted closely into the tube containing the palladium id cemented in place. A perforated palladium diaphragm, *R*, rved to prevent actual contact between the palladium and sulphur. ne detector for hydrogen sulphide, *D*, consisted merely of a small rip of filter-paper dipping in lead acetate solution. The gas as directed in a fine jet against the impregnated filter-paper and the resence of a trace of hydrogen sulphide was immediately indicated y the appearance of a spot of the characteristic colour. A small ondenser was introduced to prevent any vaporised sulphur passing ver into the detector. A second apparatus identical with the

FIG. 2.



foregoing except for the absence of the palladium activating agent was constructed and duplicate determinations made with both immersed in the same oil-bath thermostat, raising the temperature very slowly and keeping the rate of flow of the hydrogen in both the same. When the spot appeared on one detector, the temperature was noted and the heating continued until the second detector indicated that the minimal reduction temperature had been reached for the control observation. Some typical results follow:

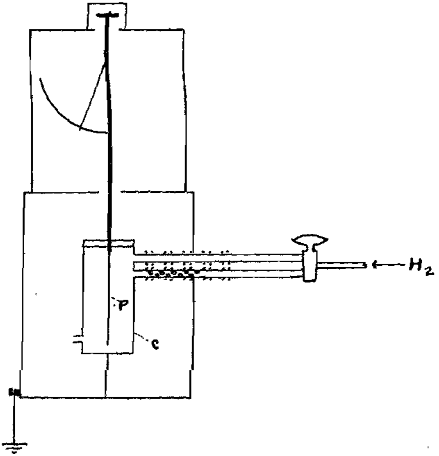
Exp.	Min. Red. Temp. of Sulphur. Control.	Pd. adjacent.
1	112·0°	80·0°
2	118·0	80·5
3	119·5	83·0

These data lend strong support to the results obtained for coppe xide.

The study of the properties of the desorbed hydrogen was coninued with a series of qualitative tests to determine whether or not he freshly desorbed gas was ionised to any degree. A gold-leaf

electroscope of the type employed by Rutherford in his radioactive measurements was used. The horizontal plate of the instrument was replaced by a small vertical plate (*p*, Fig. 3), connected directly with the gold-leaf. Around the plate and insulated from it by a sulphur plug was fixed a cylindrical brass chamber, *C*, provided with two inlet and one outlet tubes. One of the inlet tubes contained a few grams of palladium-black, and both were equally and non-inductively wound with resistance wire designed to give the

FIG. 3.



gas for "control" and "activated" tests approximately the sa temperature. Both tubes were connected with a three-way st cock leading to the pure hydrogen supply. The gold-leaf charged and the rate of the collapse of the leaf observed thro a telescope. The results obtained may be summarised in following data :

	Angle of fall.	Time in minutes.
Natural leak	1°	78
Control	1	75
Activated	1	40
Check control...............	1	78

Some experimental work was carried out at this time by Dr. J. A. Christiansen, of the University of Copenhagen, collaborating with the author at University College, with the object of determining whether or not the desorbed hydrogen could be condensed by passage through a tube immersed in liquid air. A platinum-palladium "osmosis" tube, electrically heated to a temperature at which hydrogen readily diffused through the palladium section, was employed as the activating agent, and a McLeod gauge for the delicate measurements of pressure necessary. Consistently negative results were obtained. An experiment carried out later by the author indicated that hydrogen which had undergone slow diffusion through a palladium tube exhibited no abnormal activity, a result probably to be explained by the low desorption rate. The attempted condensation could accordingly have yielded only a negative result.

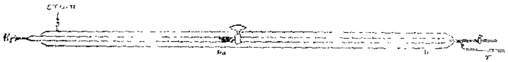
An attempt was then made to discover the cause of the activity of the desorbed hydrogen. It was considered improbable that the slight ionisation indicated by the data quoted above would account for this increased activity. The possibility of the presence of monatomic hydrogen at the temperature and pressure of the experiments was dismissed on theoretical grounds and also disproved experimentally by the interposition of a short plug of glass wool between the platinised asbestos and copper oxide in the first experiment. The reduction temperature remained unchanged, although Langmuir has shown that monatomic hydrogen is destroyed on passage through glass wool.

May the activity be explained by the presence of triatomic hydrogen? Usher (T., 1910, **97**, 400) and Lind (*J. Amer. Chem. Soc.*, 1919, **41**, 545), among others, have shown that H_3 is produced on the bombardment of hydrogen by α-rays, whilst Collie and Patterson (P., 1913, **29**, 22, 217) and Chattock and Tyndall (*Phil. Mag.*, 1908, [vi], **16**, 24) give further evidence for its formation on sparking molecular hydrogen. The positive-ray evidence of Thomson, at one time disputed, now appears to be substantiated. Wendt (*J. Amer. Chem. Soc.*, 1920, **42**, 930) furthermore attributes the activation of hydrogen by α-rays, electric discharge in a vacuum, and by the corona discharge, to the generation of triatomic hydrogen. In the absence of a positive-ray apparatus experiments were made to determine whether or not the activated hydrogen desorbed from platinum or palladium expanded on decay, as would be expected if a measurable amount of triatomic hydrogen were present: $2H_3 \rightarrow 3H_2$. An apparatus similar to a Liebig condenser was employed, with a stopcock introduced to divide the tube into two sections as shown (Fig. 4). A rapid current of live steam was

passed through the jacket, maintaining a constant temperature throughout. The entering hydrogen was preheated on passing through the left-hand section, activated on passing through the palladium-black, and decayed in the right-hand section, passing out through the capillary tube and stopcock. A small globule of mercury was introduced into the capillary side tube, T, and the apparatus adjusted at such an angle that the mercury globule was just on the point of moving down the tube under its own weight, that is, a very slight increase in the pressure within the tube would cause it to move perceptibly. A cross-hair telescope was focused on the globule and after a steady stream of hydrogen had passed for a time both stopcocks were simultaneously closed. No movement of the mercury was detected in any one of the trials, though a light oil globule was later substituted for the mercury.

The refractive index of hydrogen containing some H_3 is necessarily different from that of pure diatomic hydrogen at the same temperature and pressure. The Rayleigh gas interferometer furnishes an excellent means of detecting very slight differences in the refractive

FIG. 4.



indices of gases, and through the kindness of Messrs. Adam Hilger and Co. of London we were able to subject the activated hydrogen to this test. Interference bands were first obtained for the control setting while passing normal hydrogen through both comparator tubes of the instrument. Hydrogen activated by passage over platinum or palladium was then substituted in one of the tubes without breaking the gas flow and the position of the upper and lower bands noted. In no case was a displacement of the bands observed. The temperature and pressure of the hydrogen streams were of course kept constant. The evidence supplied by the interferometer thus reinforces that of the previous experiment in indicating the absence of a measurable amount of the triatomic modification in the desorbed hydrogen. The point can scarcely be considered as settled without a positive-ray test.

Another possible explanation of the activity of the desorbed hydrogen—an explanation to which we incline—is furnished by the concept of an increase in the internal energy of the hydrogen molecules themselves. If the Langmuir theory of adsorption on the surface of a crystal space-lattice through the bonds of residual valence is accepted, we may think of these bonds as "closing up" not instantaneously, but during a finite period corresponding with

duration of the abnormal activity. Or what is the same thing, ressed in terms of the quantum theory, the hydrogen molecule y be considered as having taken up a quantum or more of energy ing adsorption and reaching internal equilibrium only after a ɜn period succeeding its desorption.

n conclusion, it is a pleasure for the author to record his obligation l thanks to Professor F. G. Donnan, F.R.S., at whose suggestion l under whose direction this work has been carried out.

HEMICAL LABORATORIES,
UNIVERSITY COLLEGE, LONDON, [*Received, May* 15*th*, 1922.]

IOTE.—The experiments described in this paper were undertaken at the gestion of Dr. J. A. Harker, F.R.S., this suggestion being based on some liminary (unpublished) work carried out by Dr. Judd Lewis on behalf of . Colin Campbell.—F. G. DONNAN.

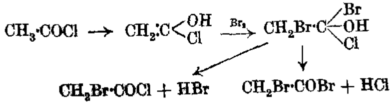
CXL.—*The Bromination of Acids in the α-Position.*

By CHARLES FREDERICK WARD.

HE mechanism of the bromination of acids in the α-position in ıe presence of red phosphorus has been supposed to necessitate ıe preliminary formation of the acid bromide, which is then ·ominated with comparative ease. In accordance with this view, atoms of bromine would be required for each molecule of the acid, ıd sufficient phosphorus to cause the formation of the acid bromide.

Lapworth (T., 1904, **85**, 41) found that pure dry acetic acid, ıturated with hydrogen chloride, was very readily attacked by romine alone with the production of monobromoacetic acid and ıat the bromination of acetone, which is supposed to involve a eto-enol transformation, was much more rapid in the presence of trace of mineral acid than in ordinary solution.

Aschan (*Ber.*, 1912, **45**, 1913; 1913, **46**, 2162) suggested that he Hell-Volhard reaction was not a case of direct substitution, ut consisted essentially in the addition of bromine to an enol orm of the acid, with subsequent loss of hydrogen bromide. He upported this suggestion by brominating acetyl chloride, when ɔromoacetyl chloride and bromoacetyl bromide were produced, a nixture of hydrogen chloride and hydrogen bromide being evolved :



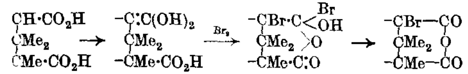
This paper contains an account of experiments made on the bromination of acetic acid, butyric acid, and camphoric acid, less bromine and phosphorus than are necessary for the production of the acid bromide being used in each case. It has been found that by using molecular proportions of the acid and bromine in the presence of a small proportion of red phosphorus (2 per cent. in most cases), good yields of α-bromoacetic and α-bromobutyric acids may be obtained directly. Camphoric acid was also treated with bromine in the presence of a small proportion of red phosphorus, and it was found that good yields of α-bromocamphoric anhydride were obtained when a solvent such as pentachloroethane was used at about 120°. At lower temperatures, in the same solvent or in a mixture of chloroform and pentachloroethane, no reaction was apparent. No reaction took place when camphoric acid was boiled with bromine in pentachloroethane solution, but the introduction of a trace of red phosphorus induced a vigorous reaction.

From these results it seems probable that the phosphorus does not act as a "carrier," but forms phosphorus tribromide, which is acted on either by the acid or by a trace of moisture which may be present, generating sufficient hydrogen bromide to bring about the enol transformation and that the reaction then proceeds along the lines suggested by Aschan (*loc. cit.*). It seems, in fact, from the experiments described later, that, unless the acid is quite free from water, the use of a considerable amount of red phosphorus is a positive disadvantage and leads to the loss of bromine by the action of the water on the phosphorus tribromide which is formed. In order to test this hypothesis, experiments were carried out on the action of bromine on acetic and butyric acids which had been treated with hydrogen bromide in the absence of any phosphorus. Good yields of the α-brominated acids could be obtained in this way, but in the case of acetic acid it was necessary to dry the acid and treat it with hydrogen bromide before use, both operations being effected by heating the acid with a small proportion of acetyl bromide.

In several experiments with acetic acid, a compound was obtained which corresponded with a substance described by Hell (*Ber.*, 1878, **11**, 244), to which he assigned the formula $(C_2H_4O_2 + Br_2)_4,HBr$. Only if the acetic acid had been dried by a chemical method did this compound, which melts at 35—40° and has a most irritating effect on the nose and eyes, decompose, when warmed at about 90°, into bromoacetic acid and hydrogen bromide. In all other cases, the substance lost bromine when warmed at 60°, probably owing to the presence of a trace of moisture.

It will be noticed that bromocamphoric anhydride is formed

ler these conditions, as in other methods for the preparation of romocamphoric acid, and it seems that the function of the trace phosphorus used is to generate sufficient hydrogen bromide to ıg about the requisite enol transformation. The enol form, ng a 1:5-hydroxy-acid, would easily give a lactone either ore or after the addition of bromine to the double bond, and the temperature of the reaction (120°) the additive compound uld lose hydrogen bromide, giving α-bromocamphoric anhydride:



attempt was also made to prepare dibromoacetic acid from nobromoacetic acid by this method, but no reaction was apparent low 120° and much charring took place above that temperature, ly a small proportion of dibromoacetic acid being isolated.

EXPERIMENTAL.

he Action of Bromine on Acetic Acid in the Presence of Varying Amounts of Red Phosphorus.

(1) Purified acetic acid (20 grams) was treated with red phosıorus (4 grams), and bromine (85 grams) gradually added. (The romine was employed in just sufficient quantity to form phoshorus tribromide and leave an excess of the halogen equivalent the acetic acid present.) The mixture having been heated at 20° for one hour to complete the reaction, the product was distilled, nd acetyl bromide (10 grams), acetic acid (5 grams), bromoacetyl romide (31 grams), and monobromoacetic acid (6 grams) were btained. After the bromoacetyl bromide had been hydrolysed, he total amount of bromoacetic acid obtained was 26 grams, or 5 per cent. of the theoretical. It seems probable that the small ield may be partly due to the action of a little water present in he acetic acid, on the phosphorus tribromide causing a loss of romine.

(2) Acetic acid (20 grams) was treated with bromine (54 grams) in the presence of red phosphorus (1 gram). The mixture was heated at about 95° and the product distilled when all the bromine had reacted. Acetic acid (4 grams), bromoacetyl bromide (5 grams), and monobromoacetic acid (28 grams) were obtained, and the total yield of bromoacetic acid after decomposition of the acid bromide was about 32 grams, or 69 per cent. of the theoretical.

(3) This was found to be the best method for the preparation of monobromoacetic acid.

Acetic acid (20 grams), to which 0·4 gram of red phosphorus had been added, was treated with bromine (58 grams) in a reflux apparatus on a boiling-water bath or preferably on a glycerol-bath at 100—105°. Much hydrogen bromide was evolved and all the bromine had reacted after about one hour. The pale brown product, which solidified on cooling, was distilled, when acetic acid (3 grams), bromoacetyl bromide (less than 1 gram), and mono bromoacetic acid, b. p. 203° (38 grams) were obtained. The yiel was about 80 per cent. of the theoretical.

This method is suitable for use with larger amounts of aceti acid, the proportions being the same as the above with a sma excess of bromine. In such cases, however, it is advisable to ad the bromine in small portions from a dropping-funnel. It is al an advantage to dry the bromine under concentrated sulphu acid before use.

Bromination of Acetic Acid in the Absence of Phosphorus.

(1) When acetic acid (20 grams), saturated with dry hydrog bromide, was treated with bromine (54 grams), the whole m solidified. The product, which melted at about 35—40°, heated at 100° for three hours, but only a little hydrogen brom was evolved. It distilled completely between 60° and 120° solidified, on cooling, to a mass of bright red crystals havin most penetrating odour and a very irritating effect on the e The substance sublimes very slowly, giving long, needle-like cryst Bromoacetic acid was not produced when the substance was tilled, because decomposition into bromine and acetic acid place at a lower temperature than that at which decompos into bromoacetic acid and hydrogen bromide occurs (Hell, *loc.*

(2) Acetic acid (50 grams, purified by freezing) was boiled acetyl bromide (3 grams) for ten minutes, the acid being thus and treated with hydrogen bromide in one operation. A mi of bromine (54 grams) and 20 grams of the prepared acid warmed at 100° for one hour, by which time all the bromin reacted. On distillation, the product yielded 38 grams of b acetic acid, corresponding with 82 per cent. of the theo yield. No bromoacetyl bromide was produced.

In all cases, about 5 per cent. of undistillable charred r was obtained.

Preparation of α-Bromobutyric Acid.

Butyric acid (15 grams), to which red phosphorus (0·4 had been added, was treated with bromine (30 grams) and

ler reflux at 120°. Much hydrogen bromide was evolved and the ıction was complete after one and a half hours. On fractionation a vacuum the mixture gave a trace of butyric acid, and then bromobutyric acid (23 grams; 82 per cent.) distilled constantly 120°/23 mm.

Bromine (1 mol.) was also added to butyric acid which had been turated with hydrogen bromide, and the mixture heated as fore. Bromobutyric acid was produced in a yield of about per cent.

he Action of Bromine on Camphoric Acid in the Presence of Small Amounts of Red Phosphorus.

(1) Camphoric acid (5 grams), carbon tetrachloride (50 c.c.), and d phosphorus (0·1 gram) were mixed and treated with bromine grams; 1 mol.). The mixture was boiled for five hours, but nly a little hydrogen bromide was evolved. The solvent and excess f bromine were removed and the residue was fractionally crystallised om chloroform and ether. It was found to be unchanged camphoric acid, m. p. 184°, only a trace of a product having a higher melting point being isolated.

(2) Camphoric acid (5 grams) was dissolved in warm pentachlorothane (30 c.c.), and red phosphorus (0·1 gram) and bromine 4 grams) were added. On boiling the solution, much hydrogen bromide was evolved, but considerable charring occurred and only a small amount (2 grams) of α-bromocamphoric anhydride, n. p. 216°, was isolated after evaporation of the solvent.

(3) A mixture prepared exactly as in (2) was gradually heated to 125°, when reaction commenced and much hydrogen bromide was evolved. After one hour, the solvent was evaporated in a vacuum and the product fractionally crystallised from ether and chloroform. The yield of α-bromocamphoric anhydride was about grams, or 75 per cent. of the theoretical.

In conclusion, the author desires to thank Professor F. S. Kipping, .R.S., for his interest in this work, and the Department of Scientific and Industrial Research for a grant which has enabled him to carry out this research.

THE CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 11th, 1922.*]

CXLI.—*The Chlorinated Dialkyl Sulphides.*

By William Jackson Pope and James Leonard Brierley Smith.

We have previously shown that propylene and β-butylene react with sulphur monochloride in just the same way as does ethylene itself, yielding dichlorodialkyl sulphides and free sulphur (T., 1921 **119**, 396) in accordance with the equation,

$$2X_2C{:}CX_2 + S_2Cl_2 = (X_2CCl{\cdot}CX_2)_2S + S \quad . \quad . \quad . \quad (1)$$

The study of the action of sulphur monochloride on homologu of the above hydrocarbons, such as *iso*amylene and β-methyl-Δ butylene, shows that under specific conditions reaction occu with formation of a true disulphide, no sulphur being liberate thus:

$$2X_2C{:}CX_2 + S_2Cl_2 = (X_2CCl{\cdot}CX_2)_2S_2 \quad . \quad . \quad . \quad . \quad (2)$$

It has been abundantly proved (T., 1920, **117**, 271; 1921, **1** 418, 634; this vol., p. 594) that ethylene and sulphur monochlor react at all ordinary temperatures in the manner indicated equation 1, although the liberated sulphur may remain in a st of "pseudo-solution"; it is now proved that at temperat below 20° *iso*amylene and β-methyl-Δ^{β}-butylene yield a disulp with sulphur monochloride in accordance with equation 2. reaction between allyl chloride and sulphur monochloride g at 100°, ββ′γγ′-tetrachlorodipropyl sulphide and sulphur, wl at temperatures below 20°, the corresponding disulphide is produced.

The disulphides now described yield the corresponding chlori alkylsulphonic acids on treatment with nitric acid, but the oxid does not proceed quantitatively; it is not possible, therefo decide whether the disulphides contain the grouping -S· >S:S, but it seems likely that the former element of consti is present, as no trace of free sulphur appears during mild oxid If the grouping >S:S were present, it might be suggested th disulphide is formed at the low temperature and decompos monosulphide at temperatures above 20°; such a view can maintained, because the disulphide produced from allyl c and sulphur monochloride below 20° may be distilled without decomposing into sulphur and the monosulphide is formed when the reaction is brought about at 100°. The disulphides now described thus do not appear to possess t of constitution ascribed by Naik (T., 1921, **119**, 379) to the ketones which he obtained by the use of sulphur mono

t are rather of the type of the ββ′-dichlorodiethyl disulphide, $H_2Cl{\cdot}CH_2{\cdot}S)_2$, prepared by Bennett (T., 1921, **119**, 418).

Experimental.

ββ′-*Dichloro-αα′-dimethyldi*iso*butyl Disulphide*, $(CMe_2Cl{\cdot}CHMe)_2S_2$.
-Amylene was prepared by passing the vapour of ordinary amyl cohol over pumice saturated with phosphoric acid, contained an iron tube heated at about 300°; the issuing vapour was passed rough a condenser, washed with 50 per cent. sulphuric acid, ried with calcium chloride, and liquefied in a freezing mixture. *he oily distillate contained about* 40 per cent. of a mixture of oamylene, $CHMe_2{\cdot}CH{:}CH_2$, boiling at 17°, and β-methyl-Δ^{β}-utylene, boiling at 37°; these were separated by fractional istillation.

The reaction between *iso*amylene and sulphur monochloride is ttended by a large evolution of heat and on passing nitrogen aturated with the hydrocarbon through a mechanically shaken eries of bulks immersed in a water-bath it was not found possible o control the reaction satisfactorily at temperatures above 20°; inder these conditions much hydrogen chloride was evolved and ı black resinous oil obtained. The addition of *iso*amylene (2 mols.) lrop by drop to sulphur monochloride (1 mol.), kept well stirred ınd maintained at –10°, resulted in the production of a pale yellow oil; this oil deposits no sulphur when kept and is entirely soluble n ether. It has no appreciable vesicant action on the skin, but its vapour causes inflammation of the mucous membrane. When heated on the water-bath, the oil darkens in colour and on distillation under 11 mm. pressure a little hydrogen chloride is evolved and ββ′-*dichloro-αα′-dimethyldi*iso*butyl disulphide* distils as a light red oil, which boils at 150—160°/11 mm.; the yield is about 30 per cent. of the theory (Found: C = 45·7; H = 7·4; S = 23·3; Cl = 23·6; *M*, in $CHCl_3$, = 263. $C_{10}H_{20}Cl_2S_2$ requires C = 43·7; H = 7·3; S = 23·3; Cl = 25·8 per cent.; *M* = 275).

The same product seems to result from the action of *iso*amylene ıd of β-methyl-Δ^{β}-butylene on sulphur monochloride, and it ɔpears probable that the former changes into the latter hydrourbon during the reaction. Dilute nitric acid attacks the sulphide ith great violence in the cold and, on boiling with 50 per cent. itric acid, sulphuric acid is formed together with a mixture of rganic acids from which no pure product could be isolated.

*αα′-Dimethyldi*iso*butenyl Disulphide*, $(CMe_2{:}CMe)_2S_2$.—When the bove dichloro-disulphide is boiled with alcoholic potassium iodide olution, hydrogen iodide and iodine are liberated; on pouring ıe product into sodium hydrogen sulphite solution, extracting

with ether, and evaporating off the ether, *αα'-dimethyldiisobutenyl disulphide* is obtained as a pale yellow oil (Found: S = 32·4. $C_{10}H_{18}S_2$ requires S = 31·7 per cent.).

ββ'-Diphenoxy-αα'-dimethyldiisobutyl Disulphide,

$$(C_6H_5{\cdot}O{\cdot}CMe_2{\cdot}CHMe)_2S_2.$$

—On boiling the dichloro-disulphide with sodium phenoxide (2 mols.) in alcoholic solution, sodium chloride separates, and on pouring into water a dark oil is precipitated, which is extracted with ether. From the ethereal solution, after boiling with charcoal, a brown oil is obtained which could not be distilled without decomposition or caused to crystallise. It is the fairly pure diphenoxy-derivative (Found: S = 17·0. $C_{22}H_{30}O_2S_2$ requires S = 16·4 per cent.).

ββ'-Dichloro-ββ'-diphenyldiethyl Sulphide, $(C_6H_5{\cdot}CHCl{\cdot}CH_2)_2S$.—Styrene (2 mols.) reacts very violently with sulphur monochloride (1 mol.), and a temperature of 200° is rapidly attained; on main taining the temperature at 30° during admixture, a pale yellow viscid oil is produced which may be partly purified by heating unde diminished pressure at 100°. The oil deposits no sulphur when kep but evidently contains this element in "pseudo-solution," becau sulphur separates on treatment with dilute nitric acid or on solutic in ether. When styrene and sulphur are allowed to interact : 100°, the resulting pale yellow oil deposits sulphur on coolin and more is deposited on boiling with ether; the amount of sulph thus recovered corresponds with about 90 per cent. of that indicat by equation 1. The oil obtained from the ethereal solution, af separation of as much of the sulphur as possible, undergoes deco position at 200° under 1 mm. pressure; it is nearly pure *ββ'-chloro-ββ'-diphenyldiethyl sulphide* (Found: S = 11·3; Cl = 22 $C_{16}H_{16}Cl_2S$ requires S = 10·3; Cl = 22·8 per cent.). The substa has a faint odour reminiscent of the chloroalkyl sulphides, and a bit astringent taste, but has no vesicant action on the skin. No p products could be isolated on oxidation with 50 per cent. ni acid.

Distyryl Sulphide, $(C_6H_5{\cdot}CH{:}CH)_2S$.—On boiling in alcoh solution with sodium β-naphthoxide, the above chloro-sulp loses hydrogen chloride and yields the corresponding ethy derivative; this was obtained as a pale yellow oil which could be distilled without decomposition (Found: S = 14·5. C_{16} requires S = 13·3 per cent.).

ββ'γγ'-Tetrachlorodipropyl Sulphide, $(CH_2Cl{\cdot}CHCl{\cdot}CH_2)_2S$.- heating allyl chloride (2 mols.) with sulphur monochloride (1 in a sealed tube at 100° for six hours and allowing to cool, the y liquid obtained deposits crystalline sulphur; when the pro is distilled, after removing the sulphur, *ββ'γγ'-tetrachlorodip*

phide passes over with slight decomposition at 181—182°/15 mm. a pale yellow oil (Found: C = 28·0; H = 3·9; S = 12·8; = 55·0. $C_6H_{10}Cl_4S$ requires C = 28·1; H = 3·9; S = 12·5; = 55·5 per cent.).

The substance has a pungent odour recalling that characteristic the chlorinated alkyl sulphides, is without vesicant action on skin, and becomes resinous on strong cooling. On prolonged ling with 50 per cent. nitric acid, the odour of chloropicrin omes apparent, and after removing sulphuric acid by means barium carbonate, the filtered solution deposits crystalline *ium βγ-dichloropropanesulphonate*, $(CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}SO_3)_2Ba$, evaporation (Found: Ba = 25·3. $C_6H_{10}O_6Cl_4S_2Ba$ requires = 26·3 per cent.). The aqueous solution of the barium salt idly becomes acid when heated; the barium salt of the hydroxy-d thus produced does not crystallise from the solution and its duction renders difficult the preparation of the pure barium t of the sulphonic acid. When the barium salt is treated with an ess of ammonium carbonate solution, the filtrate evaporated dryness, and the residue extracted with boiling alcohol, *ammon-n βγ-dichloropropanesulphonate*, $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}SO_2{\cdot}ONH_4$, is tained in colourless needles (Found: Cl = 33·2. $C_3H_9O_3NCl_2S$ quires Cl = 33·8 per cent.).

ββ'γγ'-Tetrachlorodipropyl Disulphide, $(CH_2Cl{\cdot}CHCl{\cdot}CH_2)_2S_2$.— preserving a mixture of sulphur monochloride (1 mol.) and allyl loride (2 mols.) at the ordinary temperature, the yellow colour the sulphur chloride slowly fades and after ten days a colourless, cous liquid remains. No sulphur is deposited, and, on distillation der 11 mm. pressure, slight decomposition with evolution of drogen chloride occurs. A preliminary fraction is obtained at 0—190° and at 190° *ββ'γγ'-tetrachlorodipropyl disulphide* distils a light yellow oil (Found: C = 25·2; H = 3·7; S = 22·0; = 48·6. $C_6H_{10}Cl_4S_2$ requires C = 25·0; H = 3·5; S = 22·2; = 49·3 per cent.).

The substance has a pungent odour, but is without vesicant action the skin. On oxidation with 50 per cent. nitric acid, it yields e barium βγ-dichloropropanesulphonate described above (Found: = 25·4 per cent.), and the corresponding ammonium salt (Found: = 33·0 per cent.). The preliminary fraction boiling at 170—190° entioned above proved on examination to be a mixture of the ono- and the di-sulphide.

Whilst it has already been shown by Gibson and Pope that hylene reacts with sulphur monochloride in accordance with uation 1, it is now indicated that certain ethylenic derivatives act with sulphur monochloride in the manner represented by

equation 1 at high temperatures and by equation 2 at temperatures below 20°.

One of us (J. L. B. S.) is indebted to the Department of Scientific and Industrial Research for a grant enabling him to take part in the above investigation.

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CXLII.—*The Influence of Solvents on the Velocity of Formation of Quaternary Ammonium Salts.*

By JAMES ALEXANDER HAWKINS.

MENSCHUTKIN (*Z. physikal. Chem.*, 1890, **5**, 589, and in several later papers) shows that the influence exercised by solvents on the velocity of combination of tertiary bases and alkyl haloids is very great.

The experiments which follow were made in order to test the validity of certain suggestions that have been advanced to explain the nature of the action of the solvent.

Patterson and Montgomerie (T., 1912, **101**, 26) show that change of solvent frequently affects different reactions in the same order. From this, Cox (T., 1921, **119**, 142) assumes that reactions take place by the formation of intermediate compounds or solvent–solute complexes; the velocity of reaction, being dependent on the constitution of the complex, is also dependent on the constitution of the solvent and solute.

To test this assumption, freezing-point curves of mixtures of solvent and tertiary base and of solvent and alkyl haloid were determined. Maas and MacIntosh (*J. Amer. Chem. Soc.*, 1912, **34**, 1278) and Kendall (*ibid.*, 1914, **36**, 1222) used this method for the examination of organic additive compounds. The molecular proportion is plotted against the temperature, as on the addition of one pure substance to another the melting points of both are lowered and two curves are obtained intersecting at their eutectic point. If additive compounds are formed, more than one eutectic point will be obtained.

Lewis and Lamble (T., 1914, **105**, 2330) deduced from Arrhenius's equation, $\log k_{t_1}/\log k_{t_2} = A(1/T_1 - 1/T_2)$, that "when a positive catalyst is present in large quantity a diminution of the temperature coefficient should take place," and by applying the quantum theory to the Marcelin-Rice equation, $d \log k/dt = E/RT^2$, drew

the conclusion that "any agency which increases the reaction velocity diminishes the temperature coefficient of the constant."

Lewis assumes that the critical energy increment, E, the amount of energy necessary to make an average gram-molecule react, is supplied by the absorption of infra-red radiation of a given frequency which the substance is capable of absorbing. The radiation is present in the system by virtue of its temperature.

Cox (*loc. cit.*) examined the radiation theory by a study of the temperature coefficients of several reactions in different solvents and drew the conclusion that Lewis's theory is correct where the catalyst greatly accelerates the velocity of the reaction.

Temperature coefficients and the value of E for the velocity of combination of pyridine and allyl bromide were obtained in order to investigate whether or not the influence exercised by the solvent in this reaction is due to infra-red radiation.

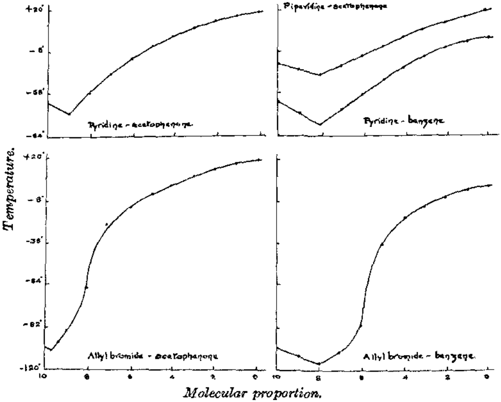
EXPERIMENTAL.

Freezing-point curves were used to determine whether or not additive compounds were formed. Temperatures from $+10°$ to $-15°$ were obtained by means of ice and salt, $-15°$ to $-70°$ by solid carbon dioxide and acetone, and temperatures lower than $-70°$ by the use of liquid air. The apparatus used resembled the usual Beckmann apparatus. The outer tube was kept at a temperature slightly lower than the freezing point of the mixture in the inner tube, which was constantly stirred. The inner tube with the mixture to be examined was contained in a slightly larger, carefully dried glass tube. This was inserted in the bath of solid carbon dioxide and acetone or liquid air, which was kept in an unsilvered Dewar flask. When the mixture had solidified, the inner tube was transferred to a dry outer tube and placed in an empty unsilvered Dewar flask, so that frostiness was avoided. The temperature was recorded when the first crystals appeared on lowering the temperature and again when the last crystals disappeared on raising the temperature.

Curves were obtained (Fig. 1) which in all cases have only one eutectic point. Consequently, no additive compounds were detected either in the case of mixtures of the tertiary base and the solvent or in the mixture of the alkyl haloid and solvent. The two solvents chosen were as diverse as possible, the reaction proceeding very rapidly in acetophenone and very slowly in benzene. The freezing-point curve of piperidine and acetophenone was also determined, as although piperidine is a secondary base its reaction with allyl bromide proceeds much more rapidly than the reaction of pyridine and allyl bromide.

From this it would appear that the reaction does not take place by the formation of intermediate compounds or solvent–solute complexes, consequently the speed of reaction cannot be determined by these solvent–solute complexes.

FIG. I.



Reaction Velocities.

Solutions of pyridine and allyl bromide in different solvents were prepared and sealed in glass tubes, the resulting solution being 0·37*N* with respect to both reagents. The quaternary ammonium salt was precipitated as a heavy red oil in all solvents except alcohol. The weight of the mixture in each tube was determined and the tubes immersed in a thermostat, the temperatures employed being 28·3°, 38·3°, and 56·5°. A tube was withdrawn at intervals and broken under water, and the ionic bromine was titrated with silver nitrate, using potassium chromate as an indicator. Time, measured in minutes, was reckoned from the moment at which the first tube was withdrawn from the thermostat, which was after a few minutes' immersion. The velocity of reaction was calculated by the formula $k = 1/C_0t \, . \, C_t/C_0 - C_t$.

All the solvents and reagents were carefully purified and dried as efficiently as possible.

Temperature 56·5°.

Solvent, toluene.			Solvent, benzene.		
Time in mins.	C_t per cent.	k.	Time in mins.	C_t per cent.	k.
87	5·88	0·00195	31	2·54	0·00229
117	8·12	0·00185	59	4·72	0·00225
162	10·00	0·00186	109	8·34	0·00227
190	11·88	0·00194			
Solvent, alcohol.			Solvent, acetone.		
25	16·32	0·0201	30	26·74	0·0328
33	20·09	0·0205	61	43·29	0·0338
66	38·75	0·0208	95	54·32	0·0337
			147	64·52	0·0334

Other results, obtained in the same manner, are tabulated below, ıe velocity constants being determined in these solvents at 28·3°, 8·3°, and 56·5°.

Solvent.	k. Temperature.		
	28·3°.	38·3°.	56·5°.
oluene	0·000231	0·000517	0·00186
enzene	0·000305	0·000642	0·00223
lcohol	0·00251	0·00557	0·0202
cetone	0·00505	0·0102	0·0338
Nitrotoluene	0·00657	0·0126	0·0376
cetophenone	0·0104	0·0203	0·0526
itrobenzene	0·0129	0·0251	0·0848

There is a very marked difference in the velocity of reaction in ıese solvents, the reaction being more than forty times faster in itrobenzene than in toluene.

Velocity of Reaction in Mixed Solvents.—Allyl bromide and yridine were added in the same concentration (0·37N) to mixtures : two solvents, and the reaction velocities were determined.

Temperature 56·5°.

Molecular proportion of solvents.			Molecular proportion of solvents.		
Acetone.	Toluene.	k.	Acetophenone.	Benzene.	k.
1	0	0·0338	1	0	0·0526
0·88	0·12	0·0224	0·68	0·32	0·0340
0·75	0·25	0·0177	0·43	0·57	0·0203
0·59	0·41	0·0124	0·19	0·81	0·00913
0·4	0·6	0·00945	0	1	0·00227
0·23	0·77	0·00687			
0	1	0·00193			

If the molecular concentration of the two solvents is plotted ;ainst the reaction velocity, it will be seen that the curve does ɔt fall off in a straight line from the highest to the lowest velocity, ıt falls slowly until a concentration is reached where the solvent which the reaction takes place more slowly, predominates to a ɪry great extent, and then drops rapidly.

From this it appears that the solvent in which the reaction proceeds more rapidly has a greater effect on the reaction velocity than that corresponding with its concentration.

Temperature Coefficients.

The usual form of expressing temperature coefficients is the ratio $(k_t + 10)/k_t$. The values of this ratio over the range 28·3° to 56·5° are given in the following table.

Solvent.	$\frac{k_{38·3°}}{k_{28·3°}}$.	$\frac{k_{56·5°}}{k_{38·3°}}$.	$\frac{k_{56·5°}}{k_{28·3°}}$.	Average ratio of $\frac{k_t+10}{k_t}$ for $\frac{k_{56·5°}}{k_{28·3}}$.
Toluene	2·25	3·59	8·05	1·97
Benzene	2·11	3·47	7·31	1·90
Alcohol	2·22	3·62	8·04	1·98
Acetone	2·02	3·31	6·69	1·82
p-Nitrotoluene	1·92	2·98	5·72	1·63
Acetophenone	1·95	2·59	5·06	1·42
Nitrobenzene	1·94	3·37	6·54	1·85

From these results it is seen that the value per degree of temperature for the ratio $k_{38·3°}/k_{28·3°}$ is slightly higher than for the ratio $k_{56·5°}/k_{38·3°}$, and this difference is in agreement with Lewis and Lamble's theory that " any agency which increases the reaction velocity diminishes the temperature coefficient of the constant."

The results, which agree, within the limits of experimental error, with the integrated formula of Arrhenius or of the radiation theory, are shown by the graph (Fig. 2), in which the logarithm of the velocity constant is plotted against the reciprocal of the absolute temperature. The slope of the line indicates the temperature coefficient.

The effect of the temperature on the velocity is better expressed by the term E, denoting the difference between the critical energy and the mean internal energy per gram-molecule, assuming that a molecule reacts when its internal energy has been raised to a certain critical value, which is generally large compared with the internal energy of the molecule. E represents the amount of energy per average gram-molecule necessary in order that the reaction may proceed: $\log k_{t_2} - \log k_{t_1} = \frac{E}{R}\left(\frac{1}{t_1} - \frac{1}{t_2}\right)$, where $R = 1·985$ calories.

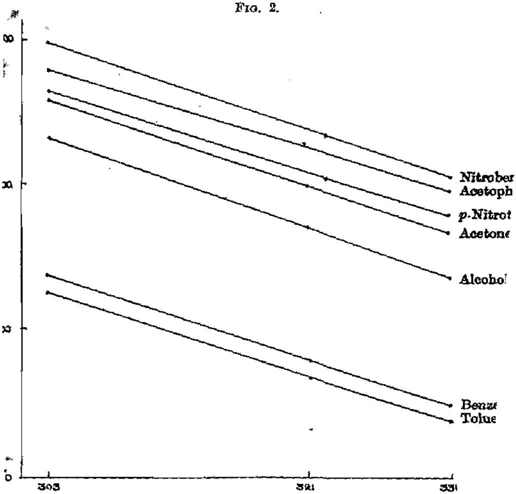
The following are the mean values of E for this reaction.

Solvent.	E	$k_{28·3°}$.	Solvent.	E.	$k_{28·3°}$.
Toluene	15,100	0·000231	*p*-Nitrotoluene ...	12,600	0·00657
Benzene	14,400	0·000305	Acetophenone ...	12,100	0·0104
Alcohol	15,100	0·00251	Nitrobenzene	13,300	0·0129
Acetone.........	13,600	0·00505			

E in these results is in the inverse order to the velocity of the reaction except in the case of alcohol and nitrobenzene. All the

other results are in agreement with the conclusion of Lewis and Lamble stated above. The temperature coefficient is not inversely proportional to the reaction velocity in different solvents, so other influences besides that of radiation must control the velocity of the reaction.

Fig. 2.



Reciprocal of the absolute temperature × 10^5.

Attempts were made to find a connexion between react velocity and the viscosity of the medium, but these were un cessful, because in this reaction the velocities are very diffe in media of nearly the same viscosity. There is some rela between the dielectric constants of the solvents and the reac velocities, the latter generally increasing in the same order as former.

Solvent.	$k_{25\cdot2^\circ}$.	Viscosity (26°).	Diele const
Toluene	0·000231	0·0053	2·
Benzene	0·000305	0·0060	2·
Alcohol	0·00251	0·0109	25·
Acetone	0·00505	0·003	21·
Acetophenone	0·0104	0·019	18
Nitrobenzene	0·0129	0·018	36

The values of the viscosities and dielectric constants of the solvents were taken from the Landolt Bornstein tables except in the case of acetophenone, the viscosity of which was determined with reference to benzene.

In the case of alcohol and nitrobenzene, where the temperature coefficients of the velocity constants are abnormally high, the dielectric constants are also abnormally high.

Summary.

1. Freezing-point curves of mixtures of solvent and tertiary base and of solvent and alkyl haloid do not disclose the existence of additive compounds, and therefore the influence of the solvent on the velocity of formation of quaternary ammonium salts is not due to the formation of such compounds.

2. The temperature coefficients of the reaction and the value of E have been determined in a number of different solvents. The results are in harmony with Lewis's theory "that any agency which increases the velocity of the reaction diminishes the temperature coefficient of the velocity constant."

3. The temperature coefficient is not inversely proportional to the reaction velocity in different solvents, so other influences besides that of radiation must control the reaction velocity.

4. There is an approximate parallelism between the dielectric constants of the solvents and the reaction velocities.

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